Ultrafast spectroscopy of natural and artificial light-harvesting systems

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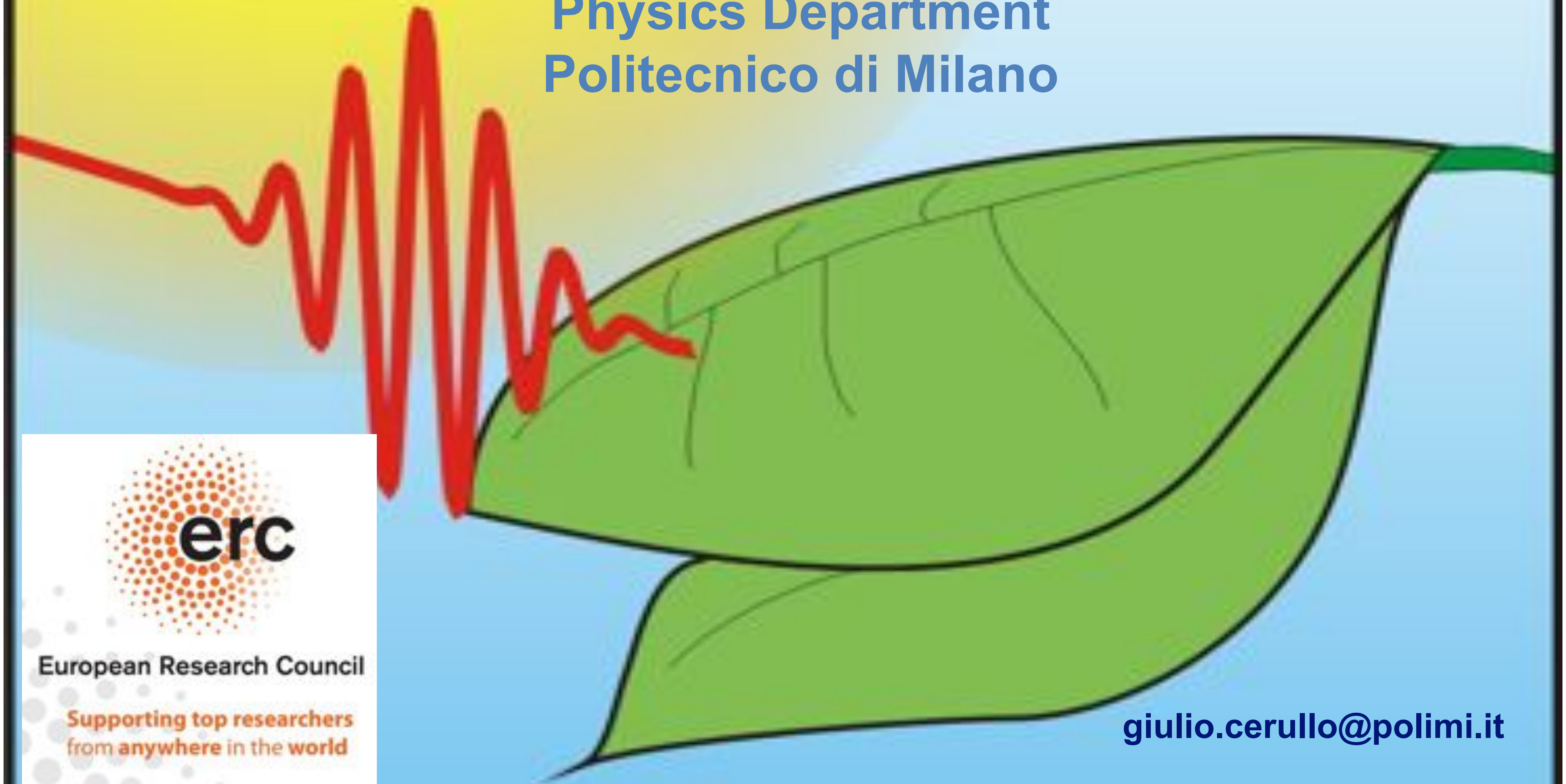

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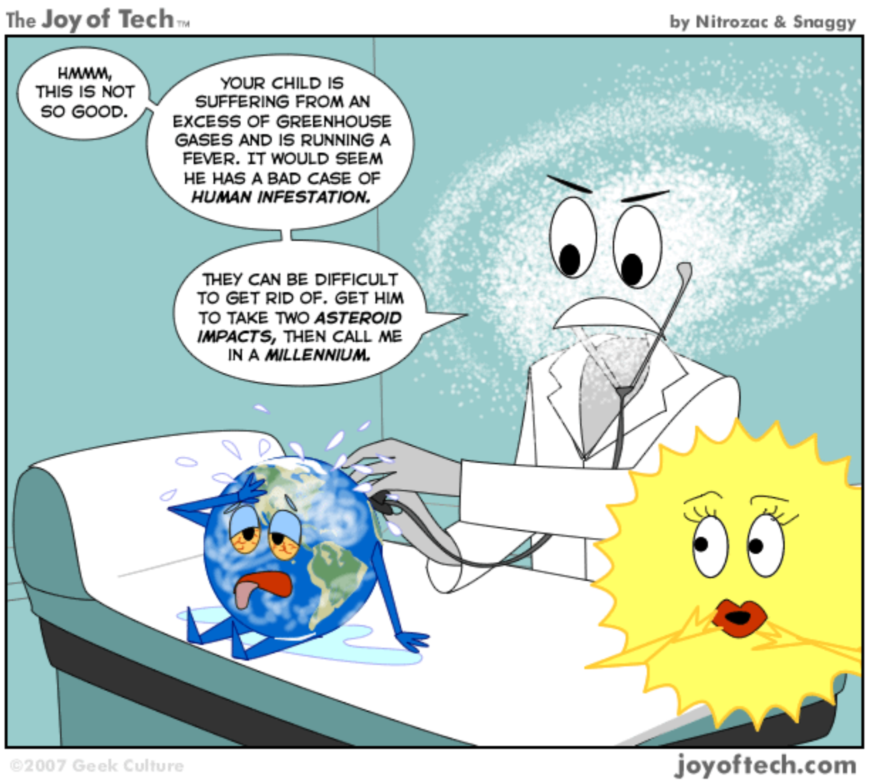
Outlook

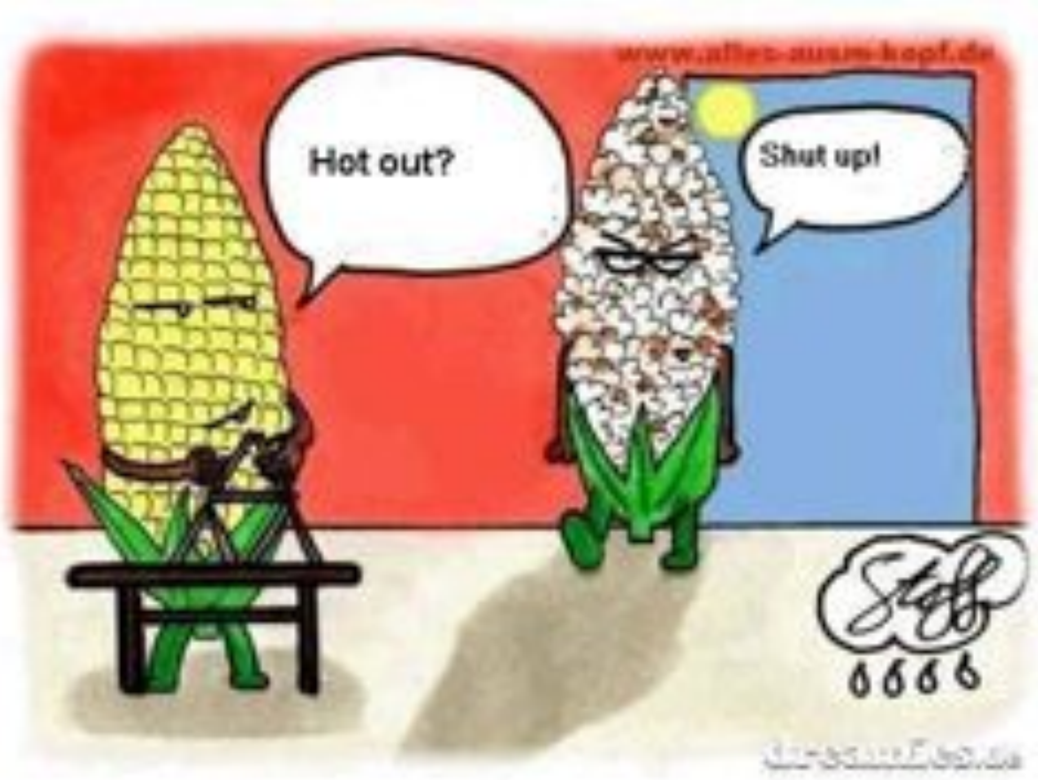
1. Photosynthetic Light Harvesting
2. Ultrafast spectroscopy
3. Natural Light-Harvesting complexes: purple bacteria
4. Artificial Light-Harvesting complexes: dyads and triads
5. Organic photovoltaic (OPV) devices: bulk heterojunctions

Earth, mankind and energy

➢ ≈**80%** of our current energy needs from **burning fossil fuels**, sufficient for only 50 to 100 years.

➢ CO_2 emission from fossil fuel combustion is the biggest source of the **anthropogenic greenhouse gas**.





"World Energy Assessment Report", United Nations (2004) http://www.undp.org/energy/weaover2004.htm

Solar energy

- We are facing a major challenge: develop **carbon-neutral, sustainable and renewable fuels**.
- Possible solution: **solar radiation** (120.000 TW!) Our needs: 15 TW.
- On average, every hour, **biomass** worth twice the mass of the **Great Pyramid of Giza** is produced.

Problems:

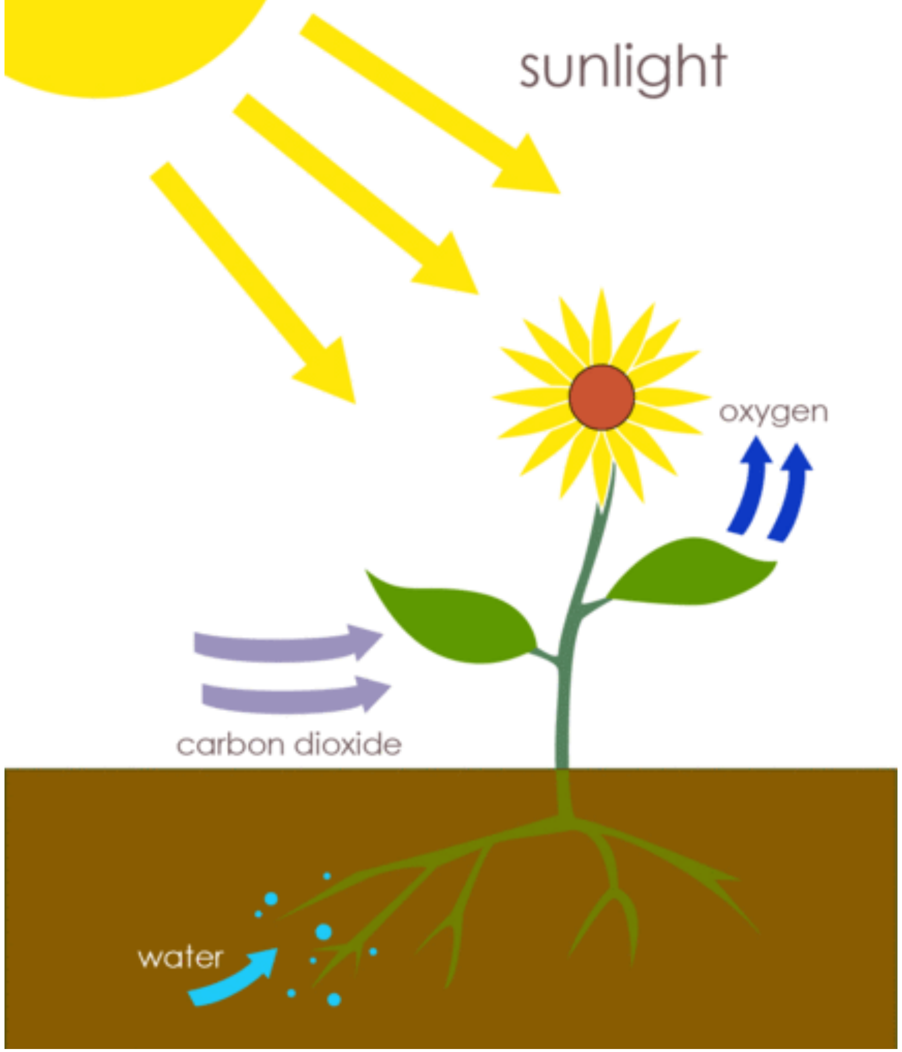
- Sunlight is **dilute**: ≈170 W/m^2 on average
- Sunlight **varies** depending on geographical location, season and weather conditions, day/night...

MRS BULLETIN **33**, 383 (2008)

Photosynthesis

$$6CO_2 + 6H_2O \xrightarrow{\text{Light}} C_6H_{12}O_6 + 6O_2$$

Carbon dioxide + Water → Sugar + Oxygen



…all of the fossil-fuel-based energy consumed today derives from sunlight harvested by photosynthetic organisms…

How to harvest sunlight energy

1) Photovoltaic cells:
energy = electromotive force
but not easily stored and used for fuel (e.g., in transportation) unless great advances in batteries.

2) Bio-inspired artificial photosynthesis
energy = chemical bonds

- **supplanting fossil fuels**
- providing **energy security**
- mitigating **climate change**

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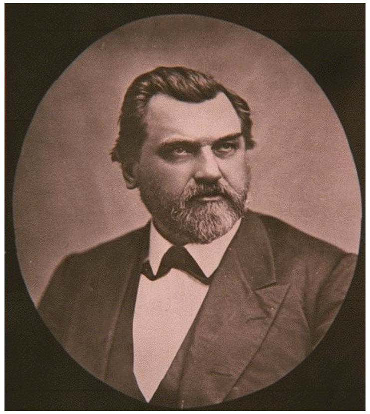
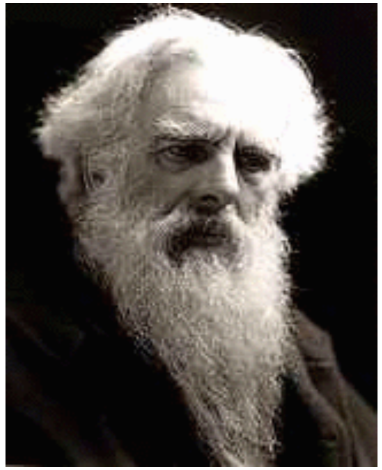
Mid-19th century painting

"A Steeplechase" by Carl Frederic Aagaard

Flash photography: "freezing in" motion



Leland Stanford



Eadweard Muybridge

Is there a time in the galloping horse´s motion when no hooves are touching the ground? Yes (flash photography, Eadweard Muybridge, 1878, 10^{-3} sec resolution)

Time resolution for molecular dynamics

POLITECNICO DI MILANO

- Atoms move with an approximate speed of $v \approx 10^3$ m/s

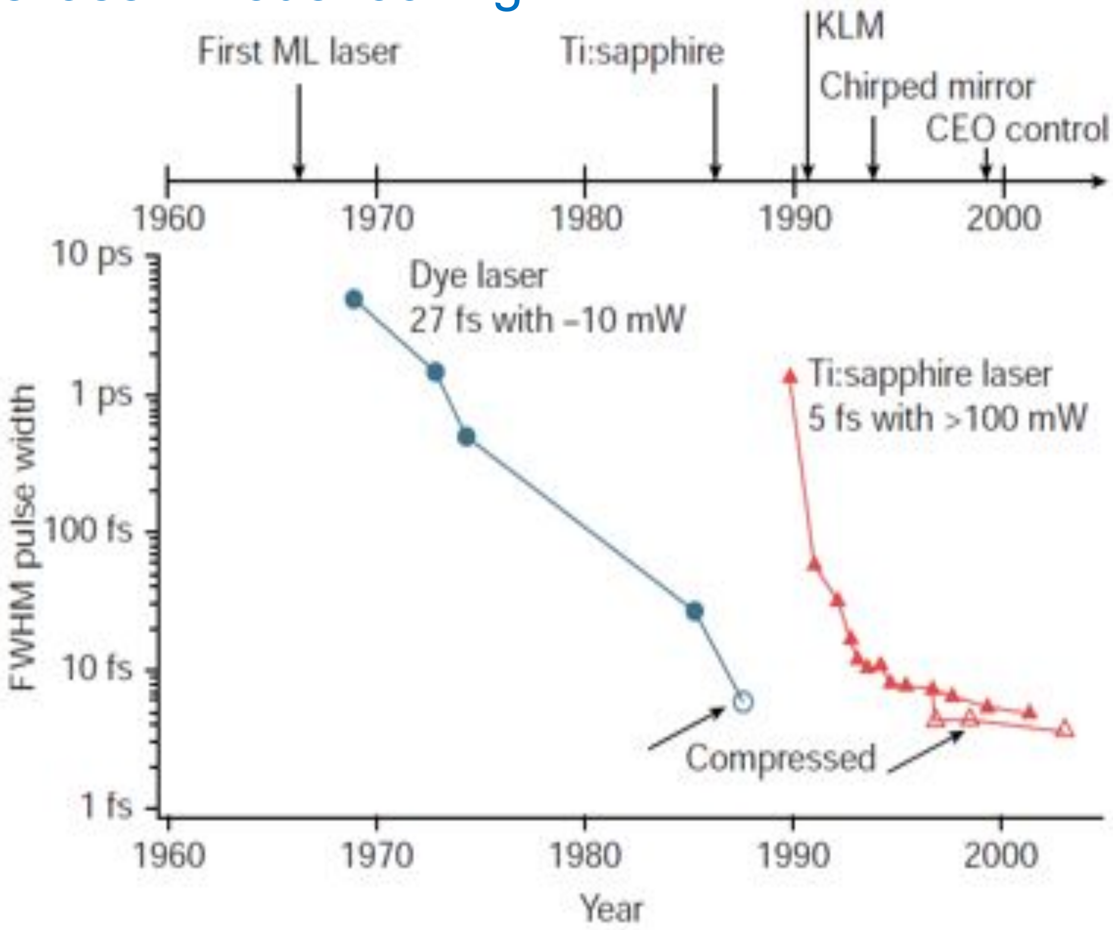
- We want to detect their motion over a length scale $d = 10^{-10}$ m

- The time resolution required is therefore:

$$\Delta t = 10^{-13}\ \text{s} = 100\ \text{fs}$$

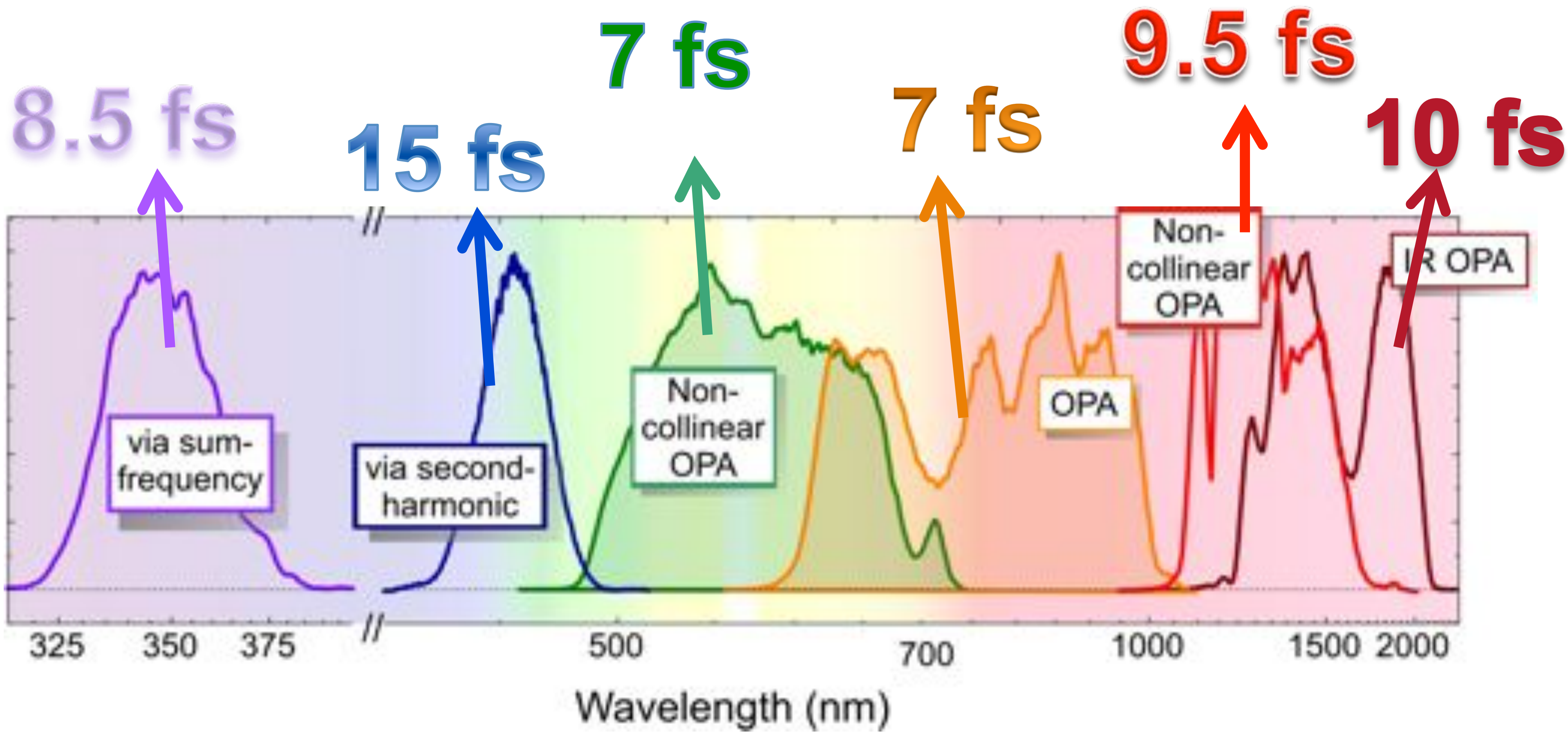
Progress in short light pulse generation

- Before the laser: Kerr shutter (10 ns)
- After the laser: mode-locking



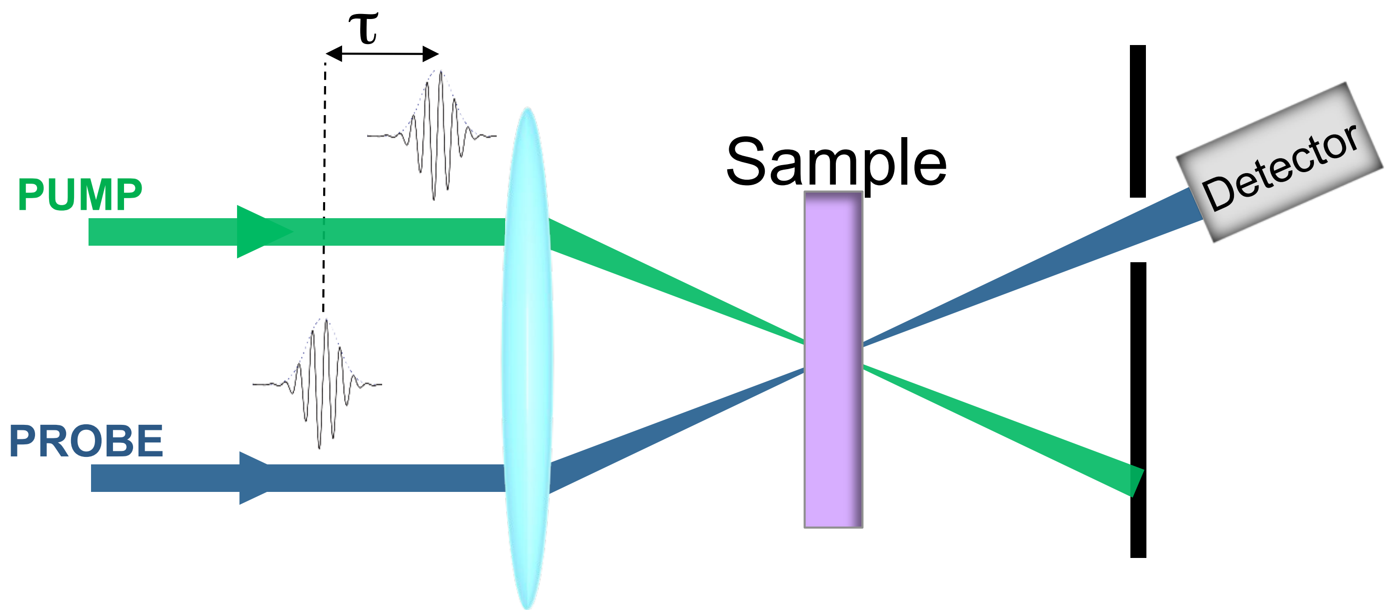
- Current pulsewidth in the visible: 4 fs (less than two periods of oscillation of electric field of light!) λ= 600 nm $\Rightarrow$ T = 2 fs

Ultrabroadband Pulse Generation



D. Brida, C. Manzoni, G. Cirmi, D. Polli, and G. Cerullo, IEEE J. Sel. Top. Q. Electron. **18**, 329 (2011).

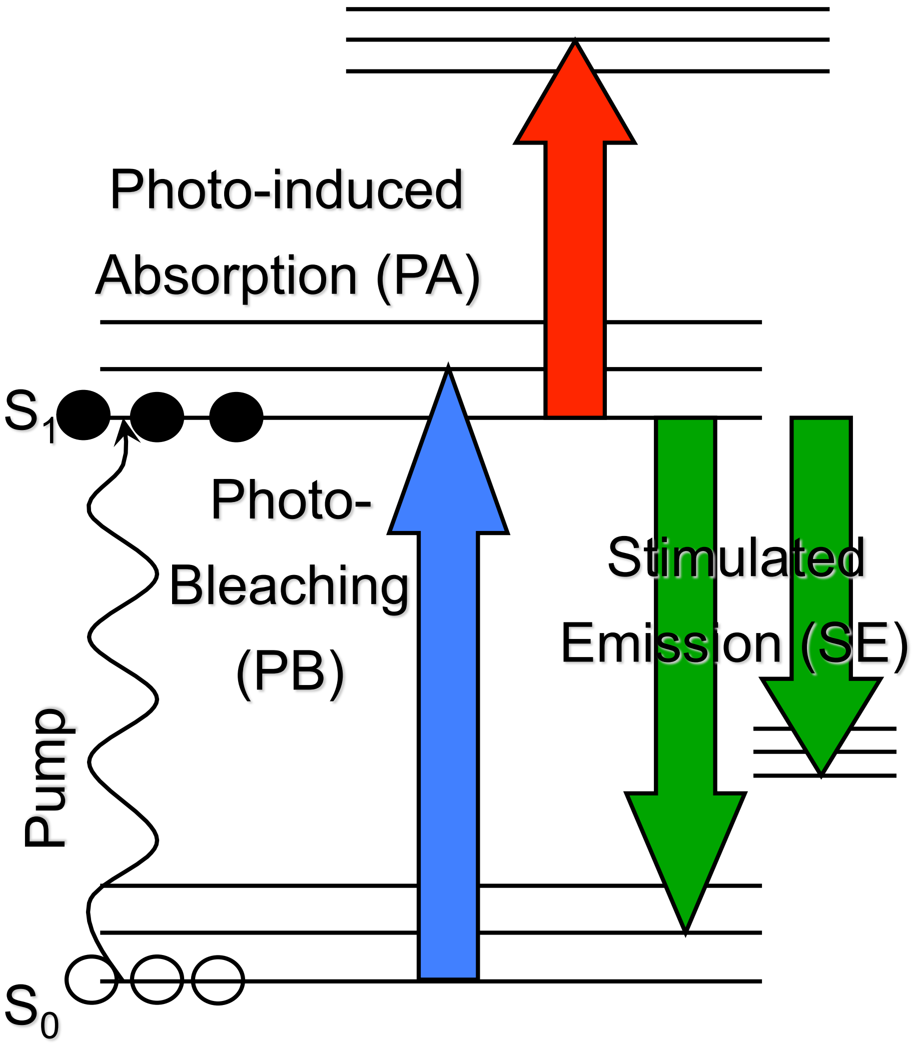
The "pump-probe" technique



- A first **pump** pulse resonantly excites the system
- A second, delayed **probe** pulse detects the pump-induced differential transmission changes:

$$\frac{\Delta T}{T} = \frac{T_{ON}(\lambda_{pr},\tau) - T_{OFF}(\lambda_{pr},\tau)}{T_{OFF}(\lambda_{pr},\tau)}$$

Pump-Probe Signals



Photobleaching (PB):

less molecules in the ground state

⇒ increased transmission $\Delta T/T>0$

Stimulated emission (SE):

from molecules in the excited state

⇒ increased transmission (gain in the sample) $\Delta T/T>0$

Photoinduced absorption (PA):

from excited state to higher states

⇒ decreased transmission $\Delta T/T<0$

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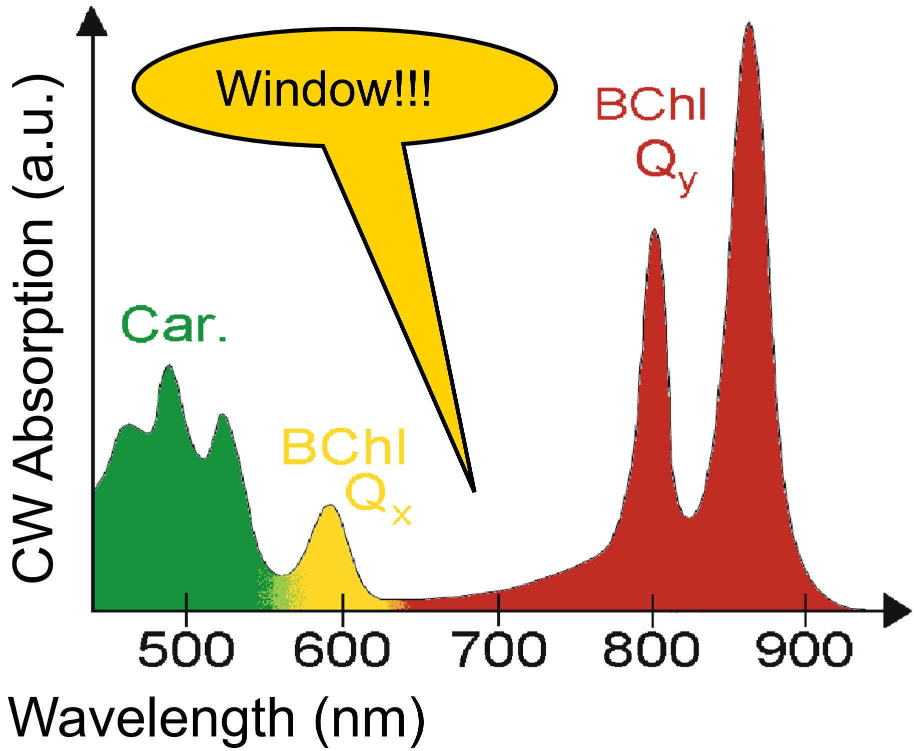
Grand Prismatic Spring (Yellowstone National Park)
Brilliant orange algae and bacteria (carotenoids and chlorophylls)

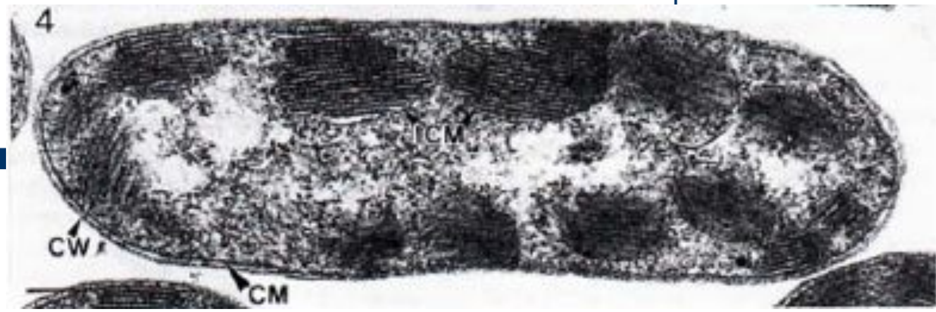
Purple photosynthetic bacteria

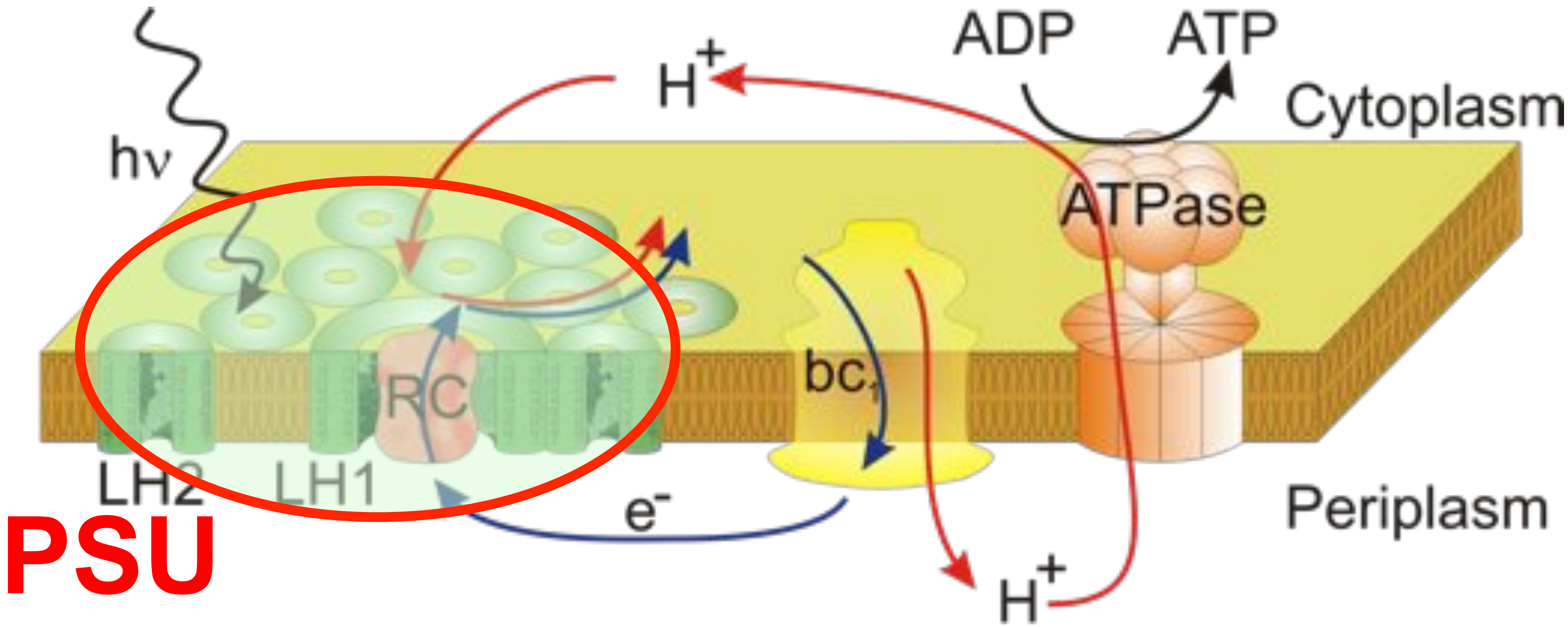


Anaerobic prokaryotes.

Excellent **model organisms** for investigating the basic mechanisms of photosynthetic light harvesting.

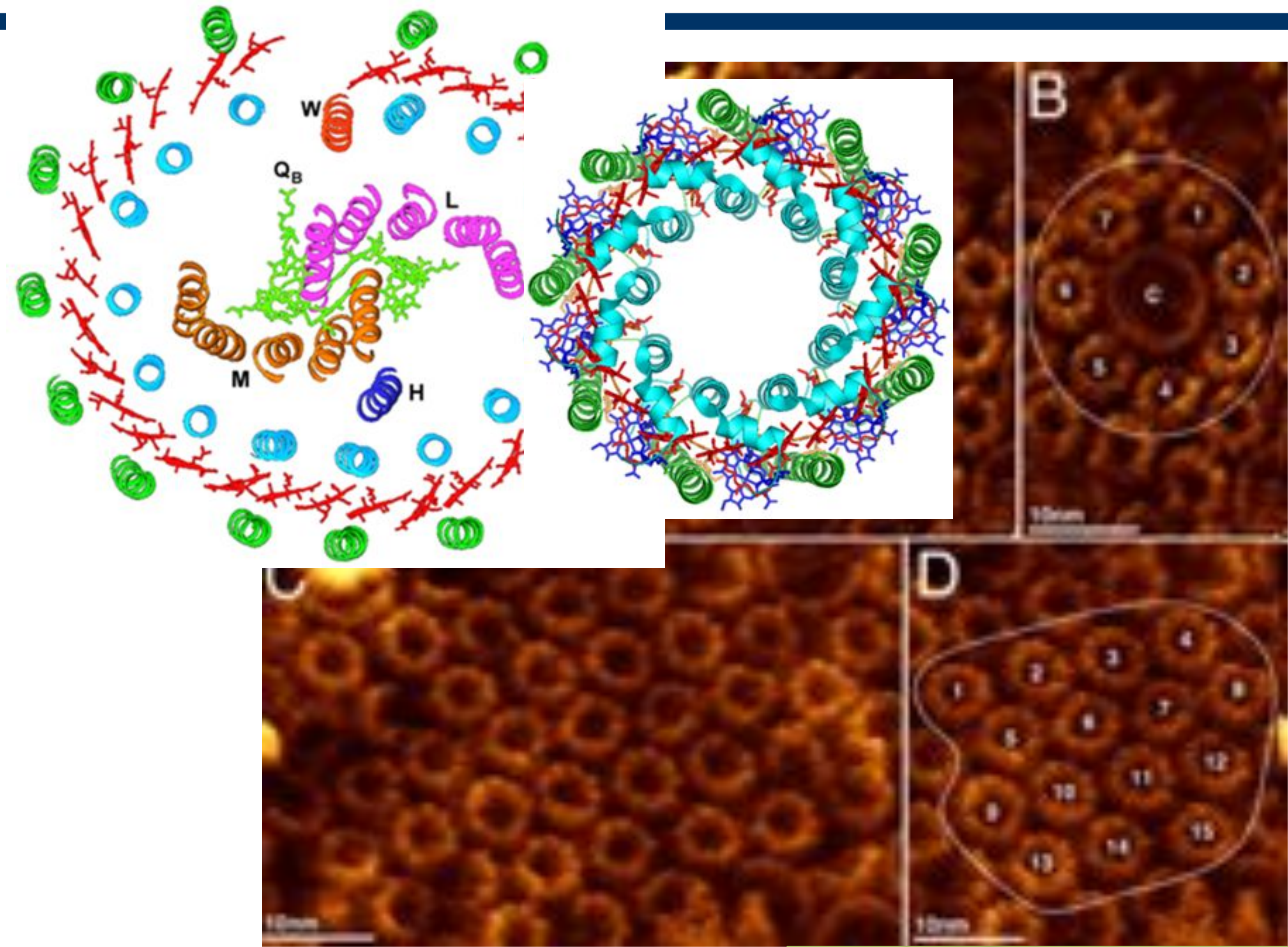
Bacterial membrane





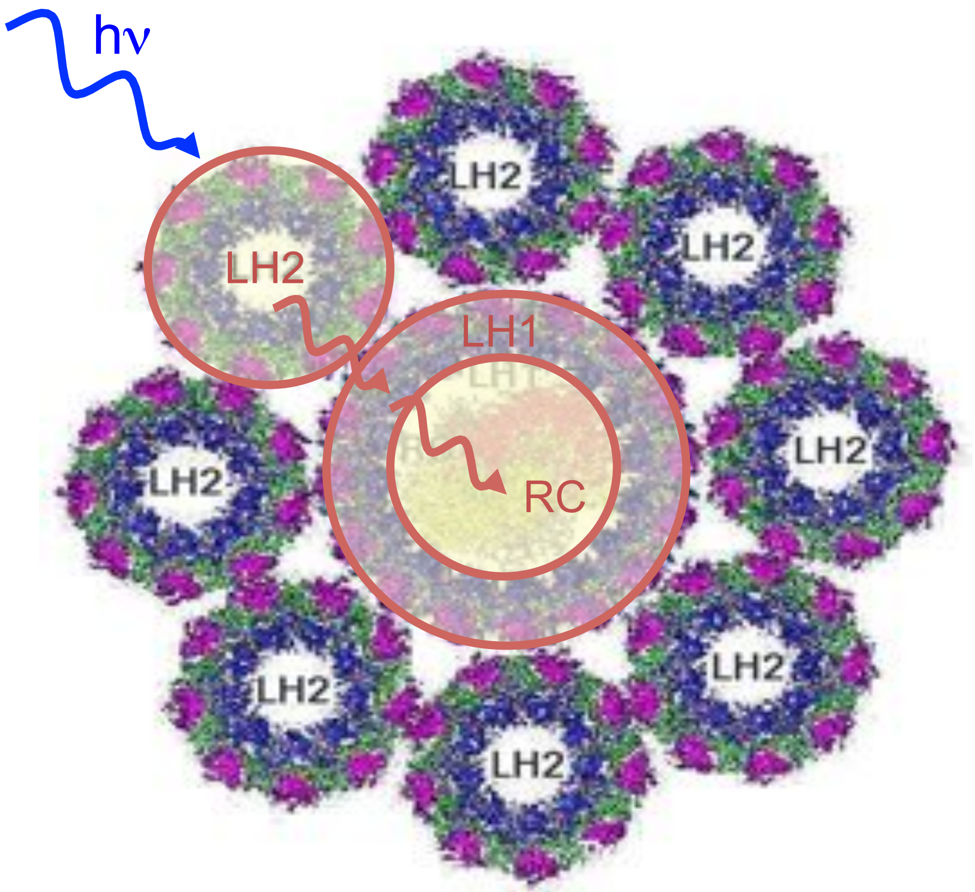
Light absorbed by the pigments in the **peripheral LH1 and LH2 complexes** induce an **energy transfer** process towards the **reaction center** (**RC**), where **charge separation** occurs. Several enzymes facilitate **electron and proton pumping** through the membrane, which in turn provoke **synthesis of ATP** from ADP in the **ATPase**.

LH1/LH2 distribution



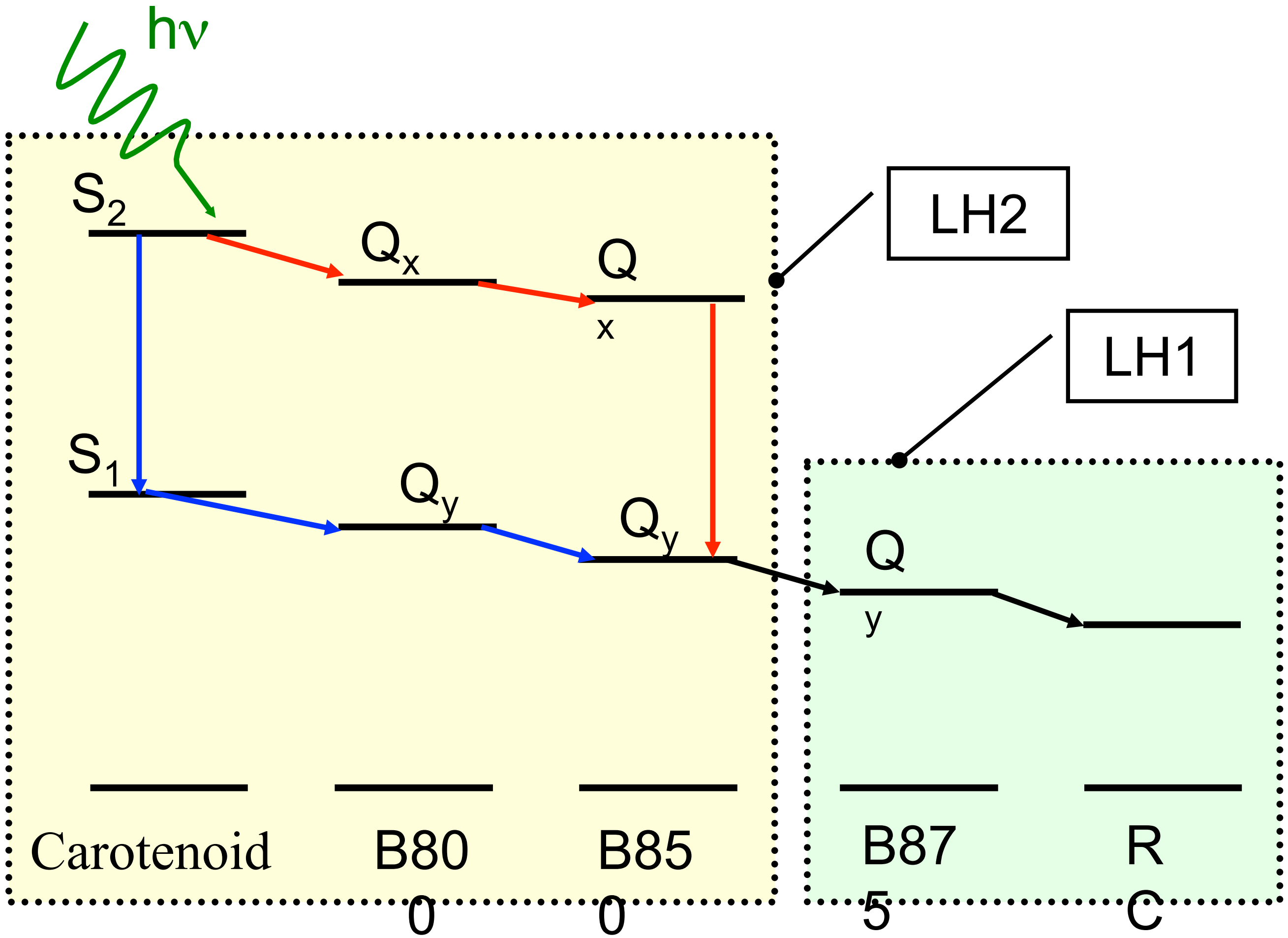
Journal of Structural Biology **159**, 278 (2007)

The Photosynthetic Unit



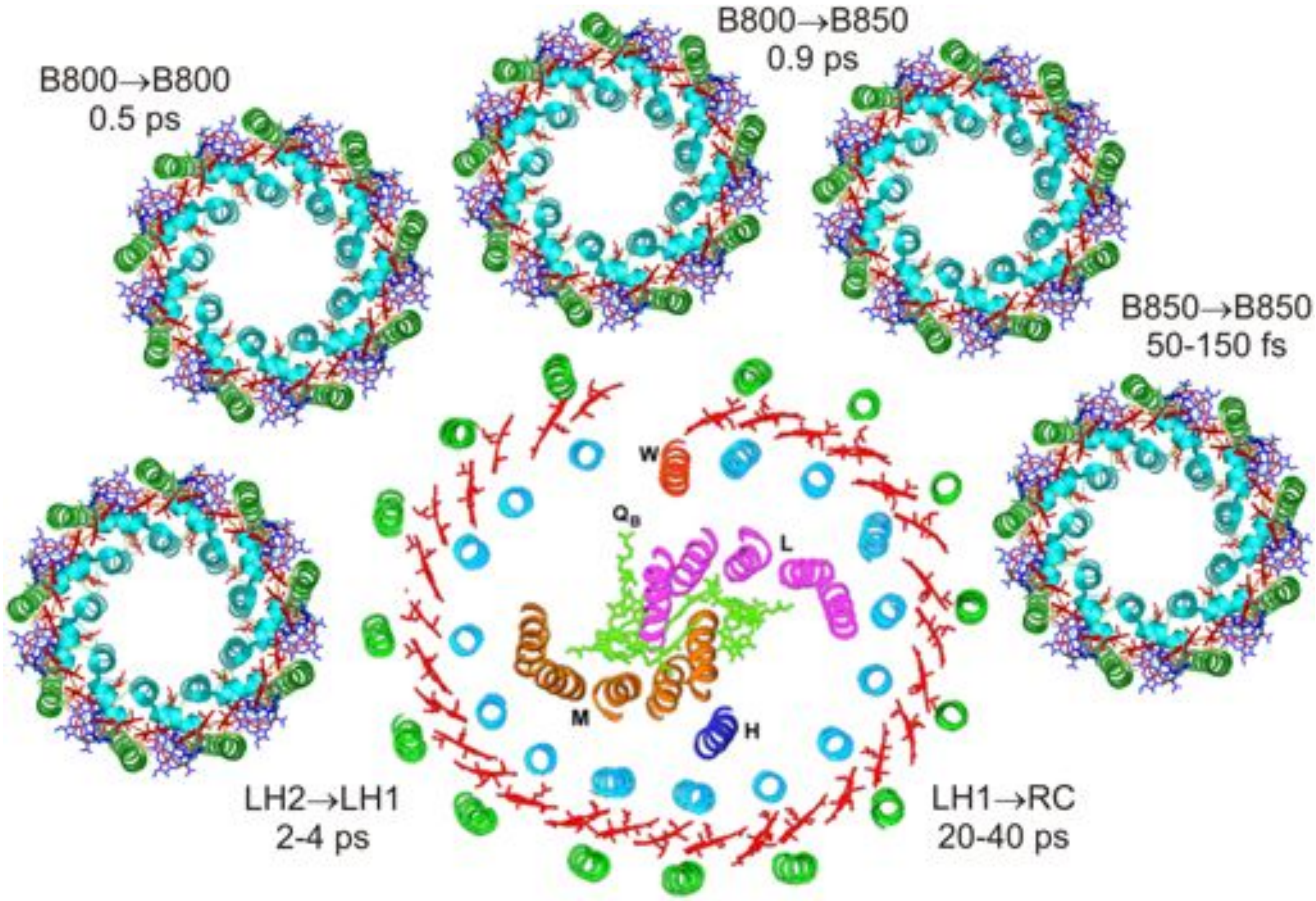
G. McDermott *et al.*, Nature 374, 517 (1995)

Fine Excitonic Tuning

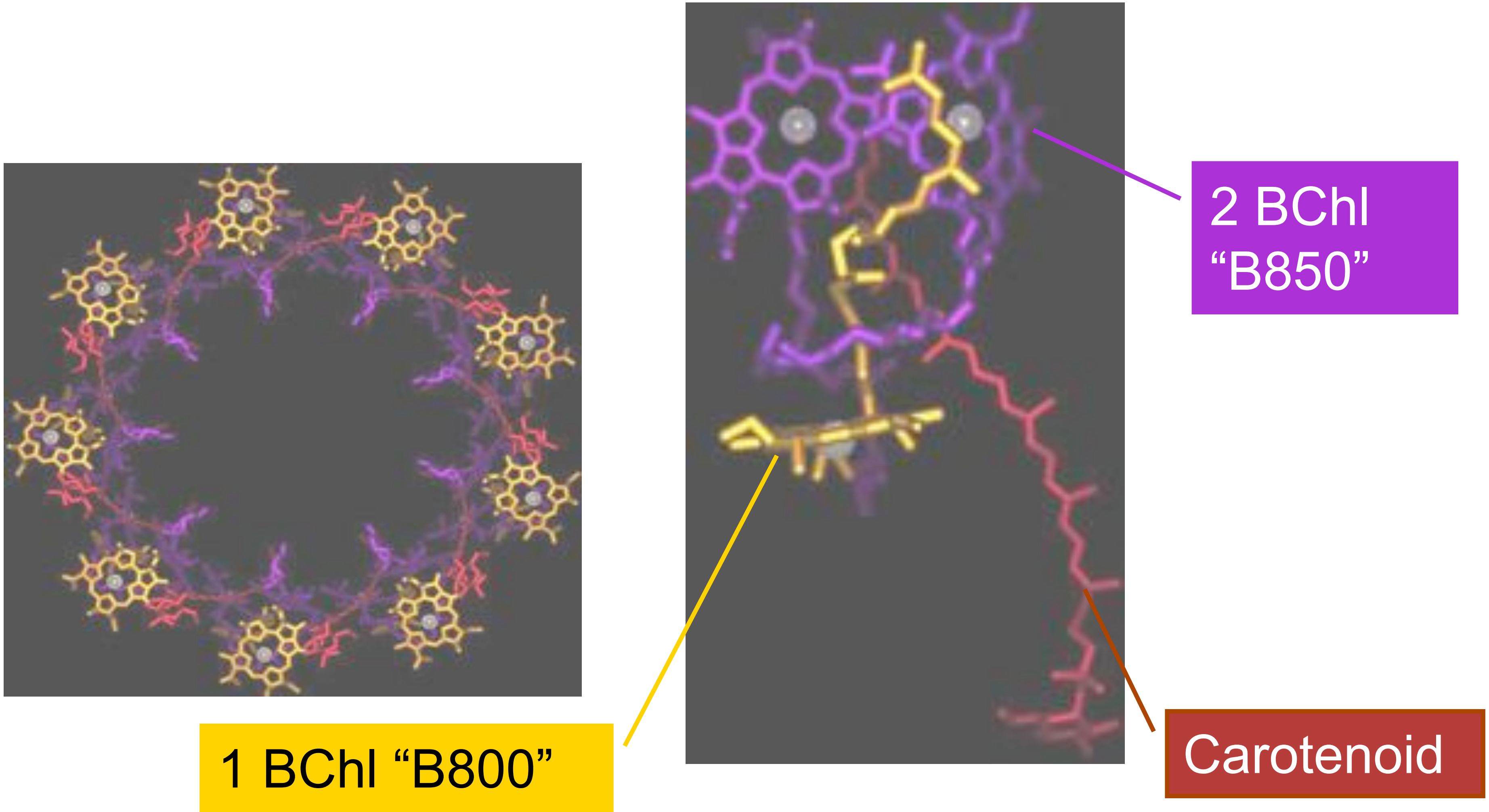


Light harvesting complexes (LH1 and LH2) absorb photons and transfer energy to the reaction center following an **energy cascade**.

Energy transfer processes



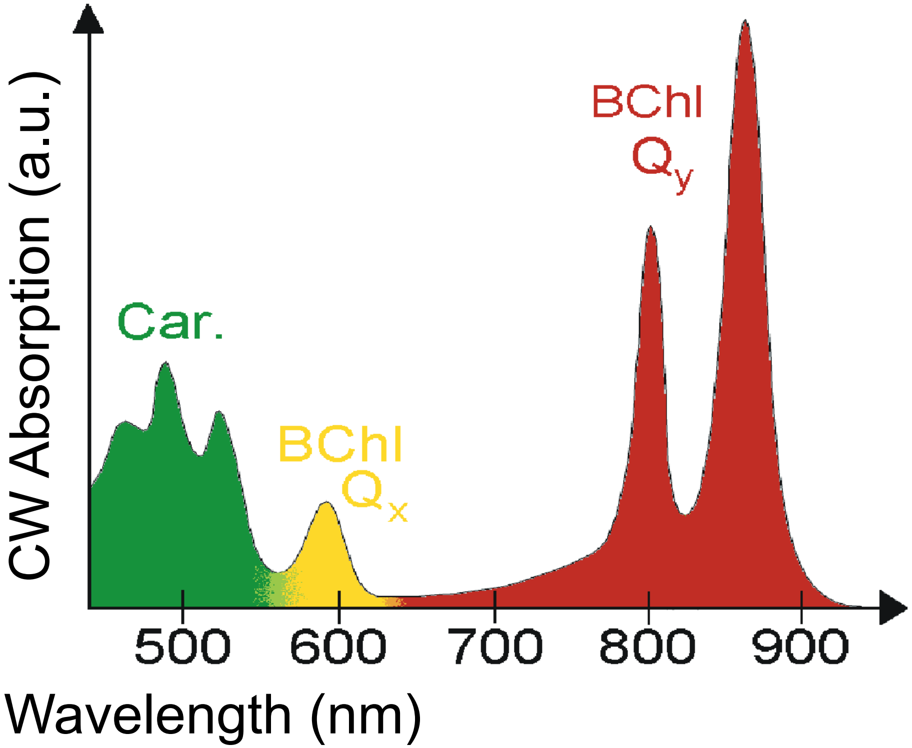
LH2: Building Blocks

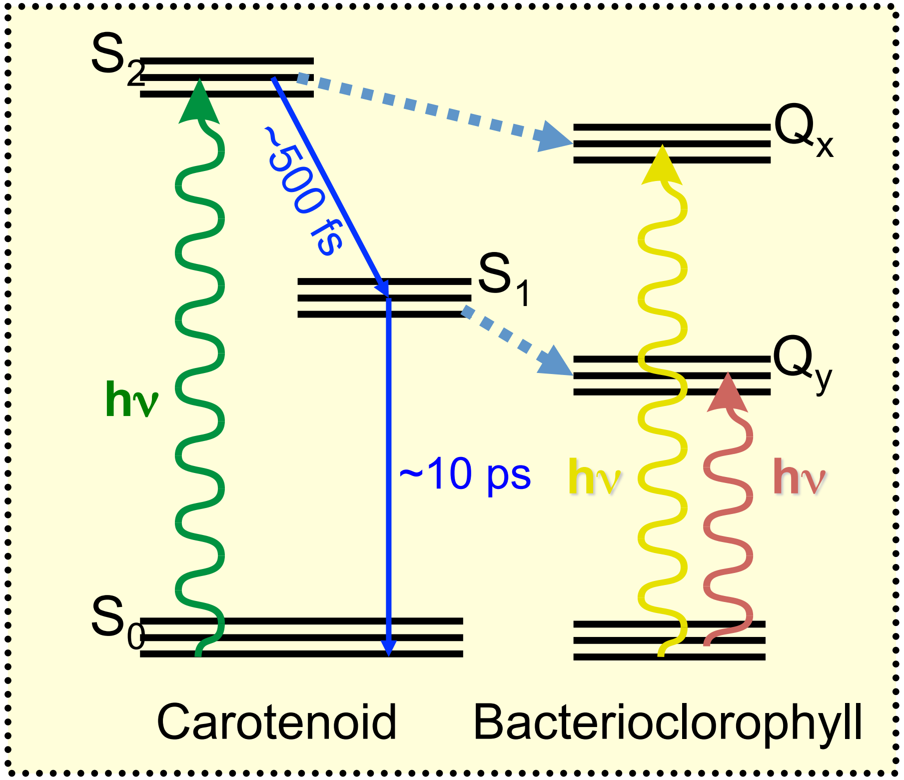


LH2 is made of **9 units**, each consisting of one **carotenoid** and three **bacterio-chlorophylls**

Nature **374**, 517 *(1995)*

LH2: Energy Transfer Steps

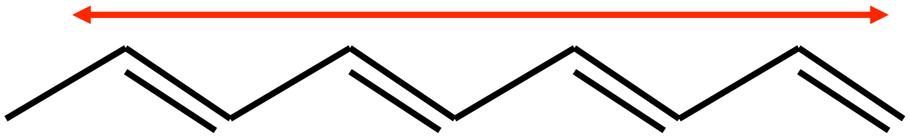




- **Energy transfer** from carotenoids to chlorophylls is the first step of photosynthesis.
- It can take place from S_2, S_1 or from a mixture of both

Carotenoids

- Carotenoids belong to the family of polyenes, linear chains of conjugated carbon atoms, joined by alternating single and double bonds



H. A. Frank, R. J. Cogdell, *J. Photochem. Photobiol.* **63**, 257 (1996).

Autumn colors

Lower risk for human cancers

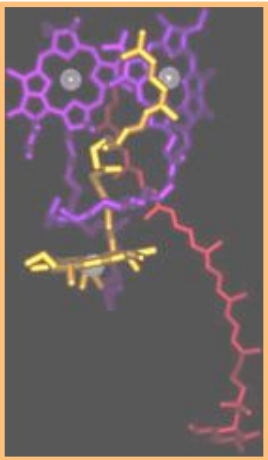
Colorful carotenoids as decoration

Role of carotenoids

- **Light harvesting** and **energy transfer** to bacteriochlorophylls

- **Dissipation** of excess energy (Non-Photochemical Quenching, NPQ)

- Structure **stabilization**

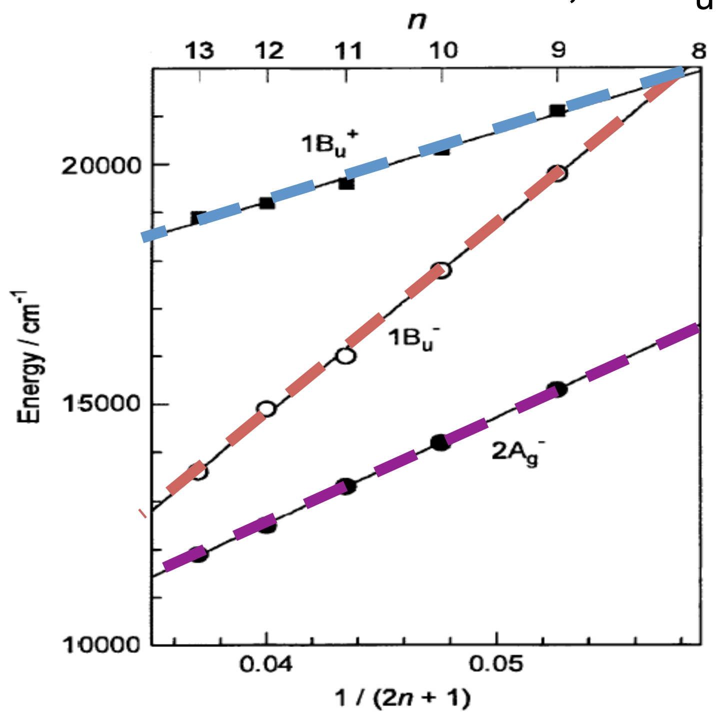


- **Photoprotection** from oxygen (oxidizing agent)

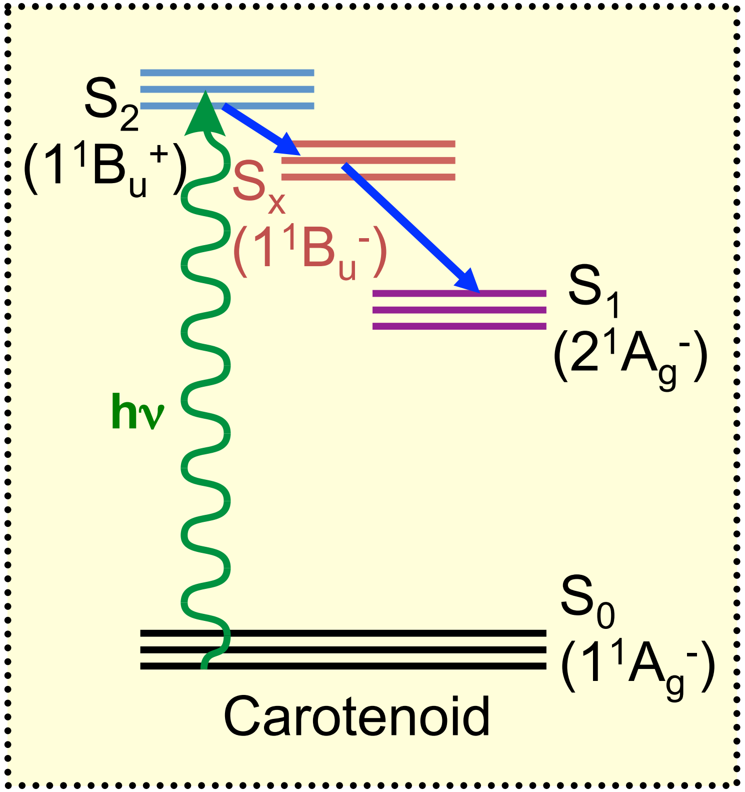
1) $^{3}BChl^{*} + {}^{3}O_2 \rightarrow {}^{1}BChl + {}^{1}O_2^{*}$
2) $^{3}BChl^{*} + {}^{1}Car \rightarrow {}^{1}BChl + {}^{3}Car^{*}$
3) $^{1}O_2^{*} + {}^{1}Car \rightarrow {}^{3}O_2 + {}^{3}Car^{*}$

The "Intermediate" State

- Quantum chemical calculations proposed the existence of **an intermediate state**, of B_u^- symmetry, between S_2 and S_1

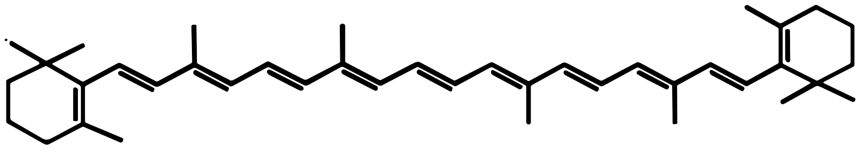


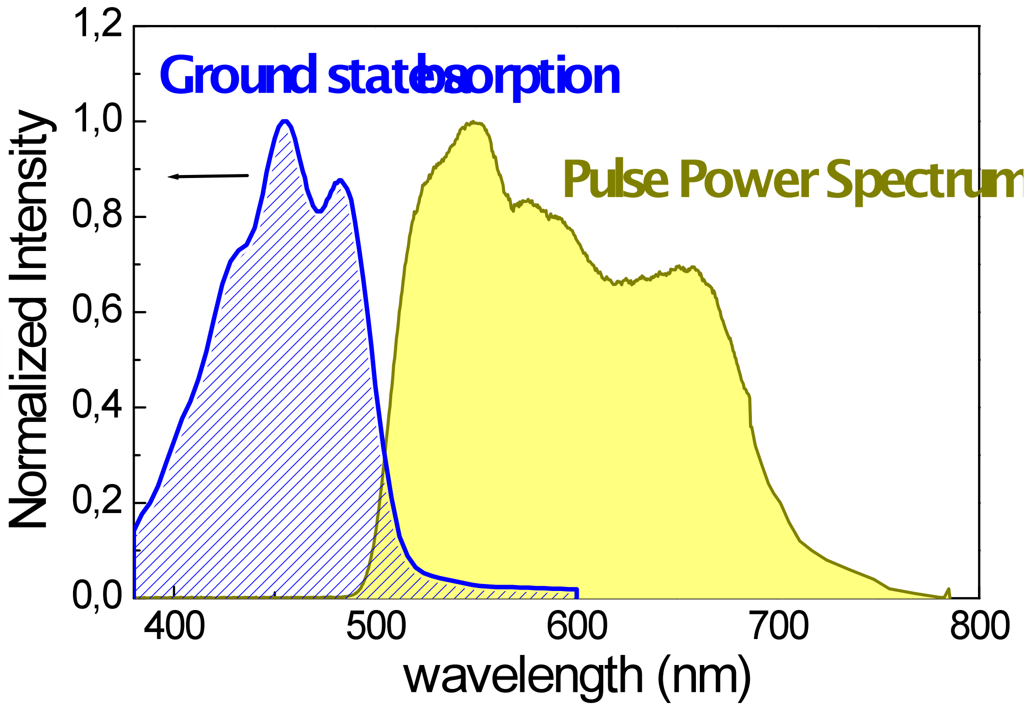
P. Tavan, K. Schulten, *Phys. Rev. B* **36**, 4337 (1987)



- $S_2 \rightarrow S_x$ energy transfer should be **extremely fast** (tens of femtoseconds)
- In spite of indirect experimental suggestions, **no clear evidence** of the existence of this state has been presented

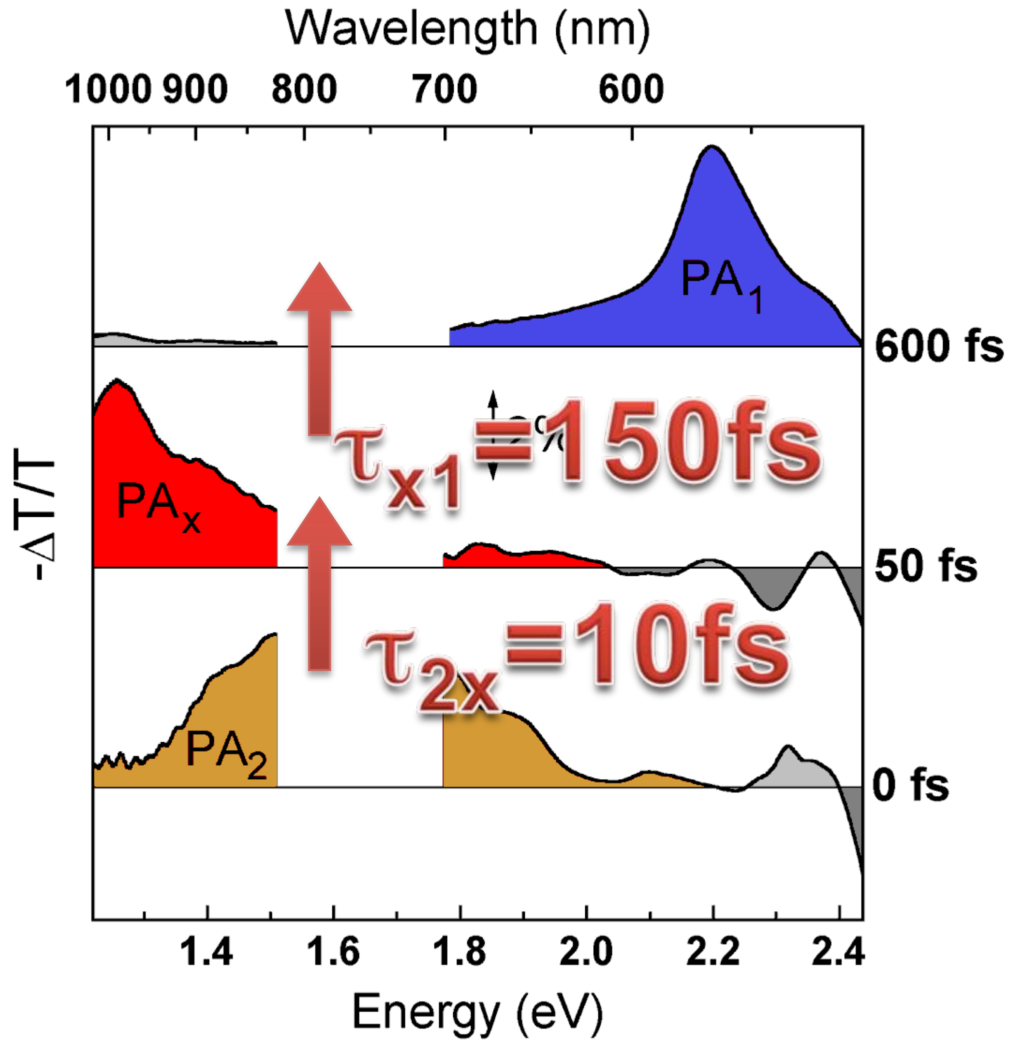
A Prototype System: β-carotene

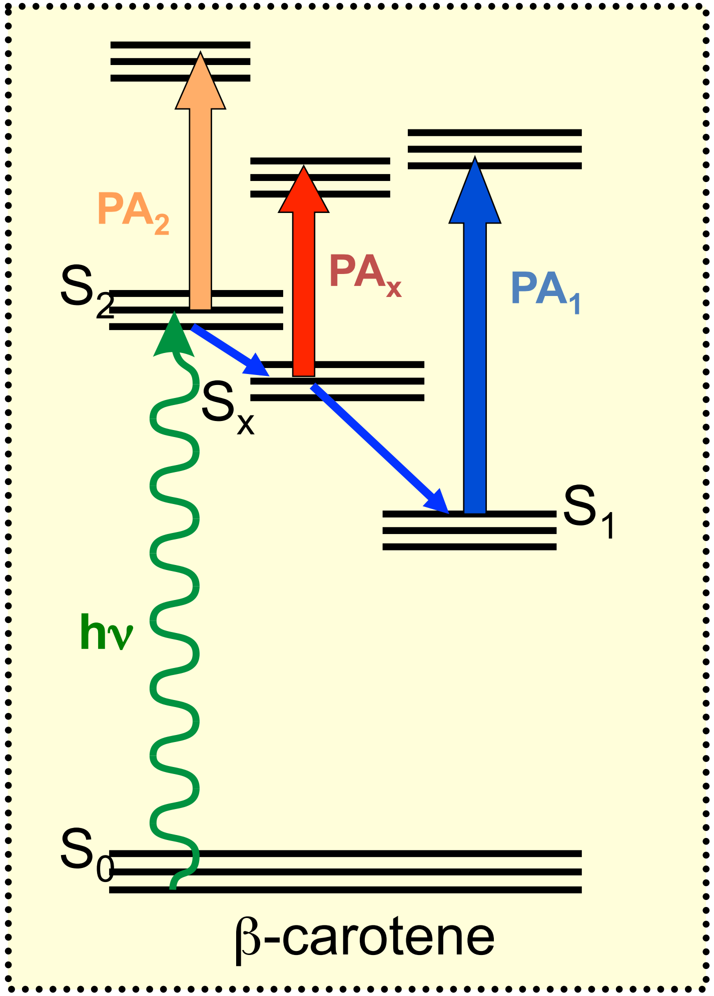




- Widespread natural **pigment**.
- 11 double bonds (9 on the chain + 2 on the terminal rings)
- Absorption in the blue-green region of the spectrum

First Steps of Internal Conversion

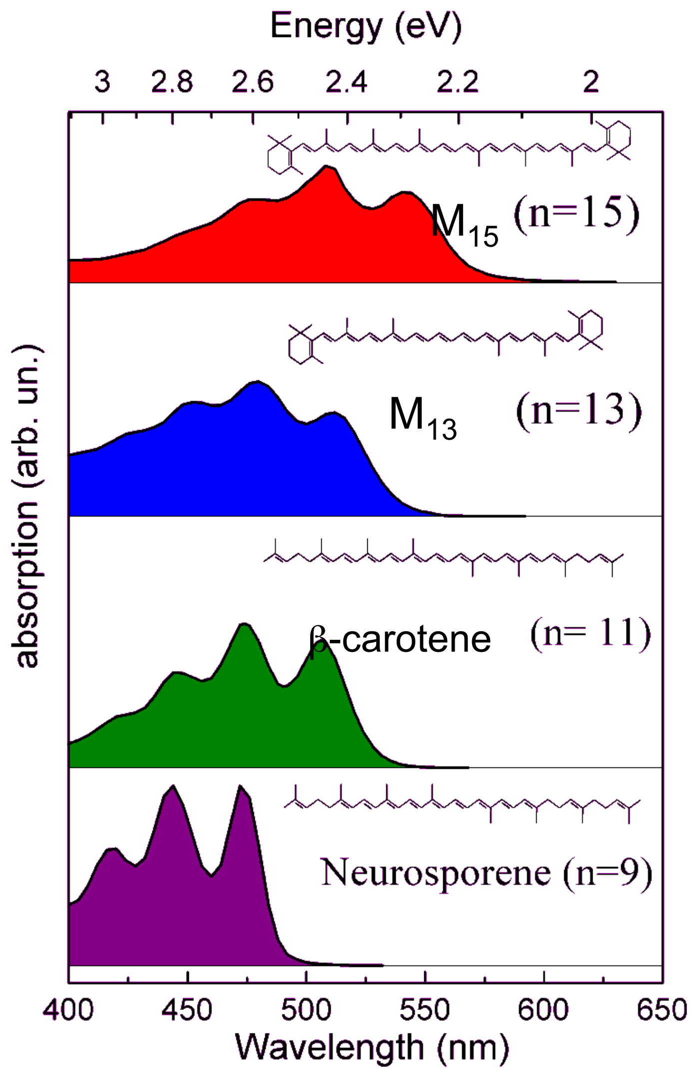




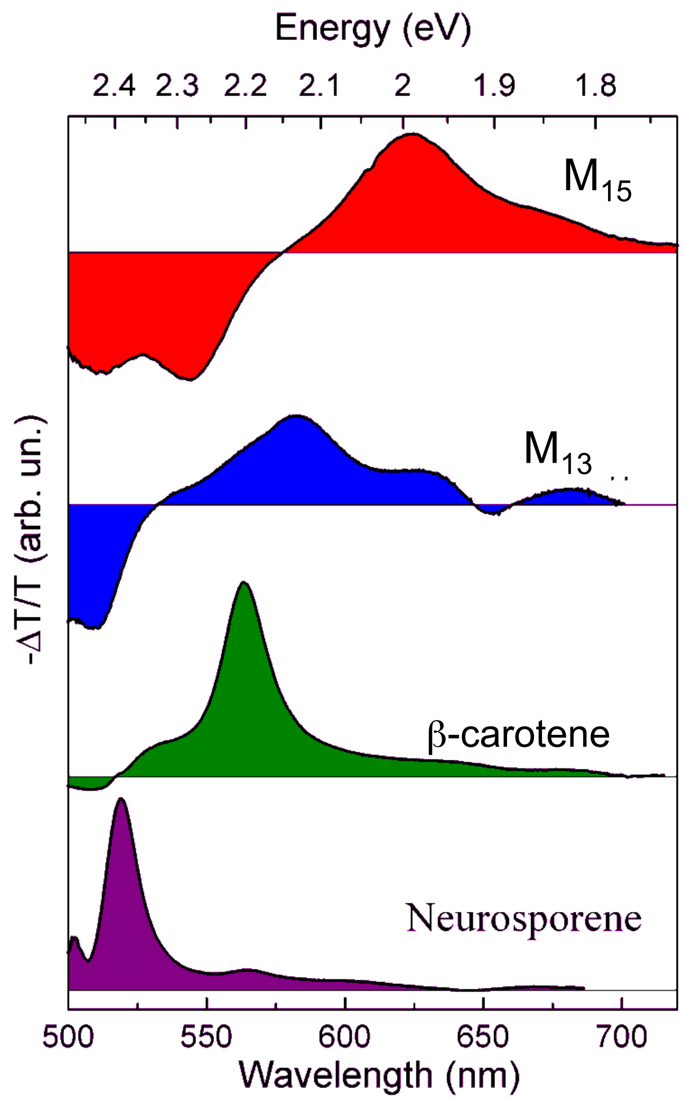
G. Cerullo, D. Polli, G. Lanzani, S. De Silvestri, H. Hashimoto, R.J. Cogdell, *Science* **298**, 2395 (2002)

Conjugation-length dependence

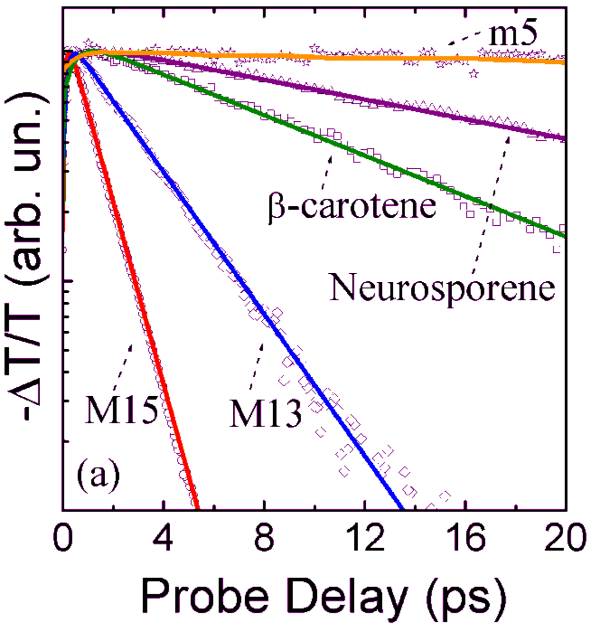
Ground-state absorption

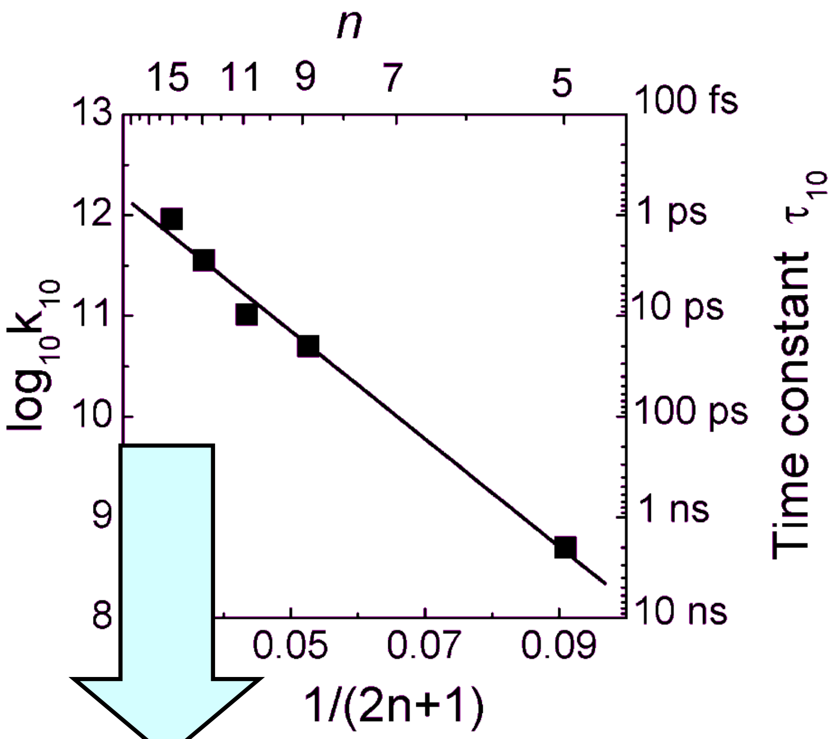


Excited-state absorption



S_1 decay dynamics





S_1 decay in accordance with the **energy gap law** for radiationless transitions in large molecules:

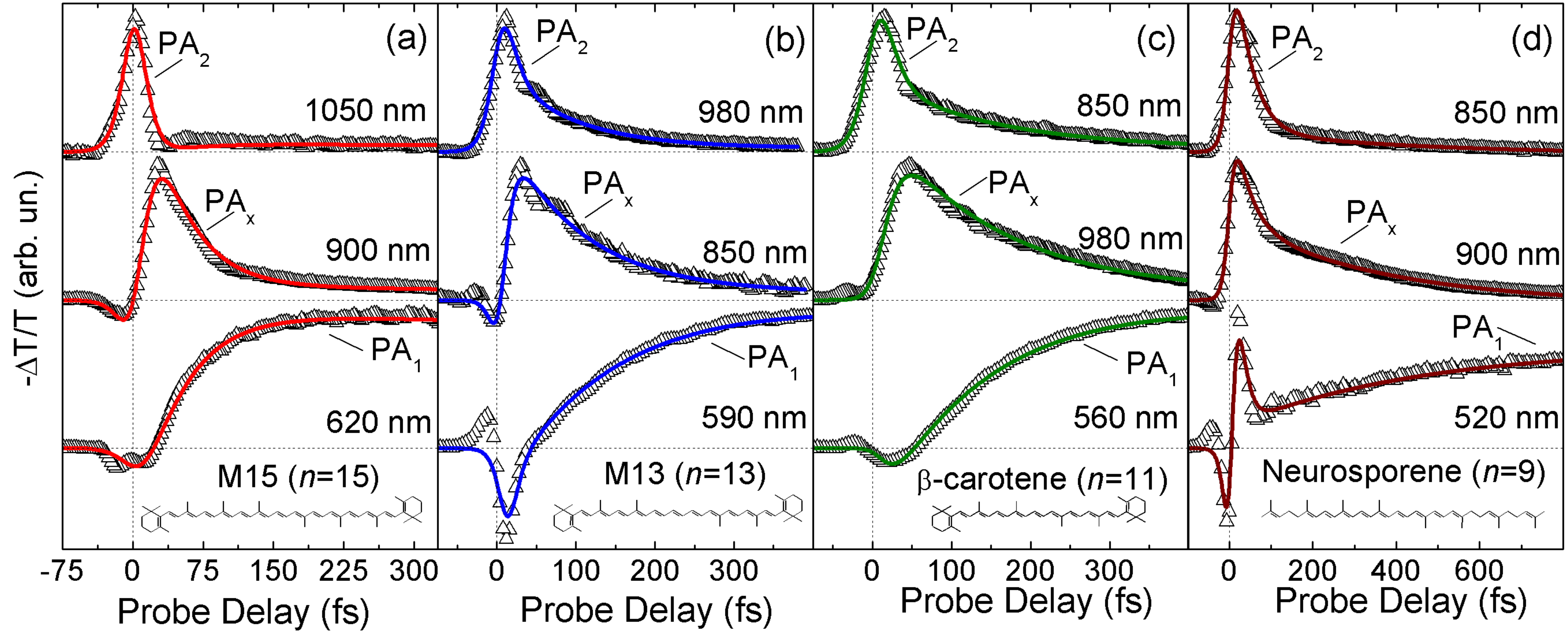
$$k \div \exp(-\beta \Delta E)$$

coefficient related to the vibrational frequency coupled to the electronic levels.

energy gap

V. Chynwat and H. A. Frank, Chem. Phys. **194**, 237-244 (1995)
O. Andersson and T. Gillbro, J. Chem. Phys. **103**, 2509 (1995).

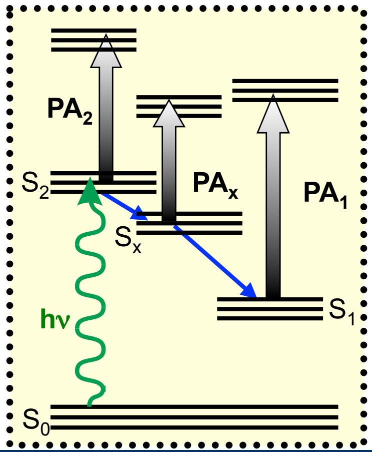
S_2 decay dynamics



- Carotenoids with n≥9: **4 excited states** are needed to explain the $S_2 \rightarrow S_1$ decay dynamics.

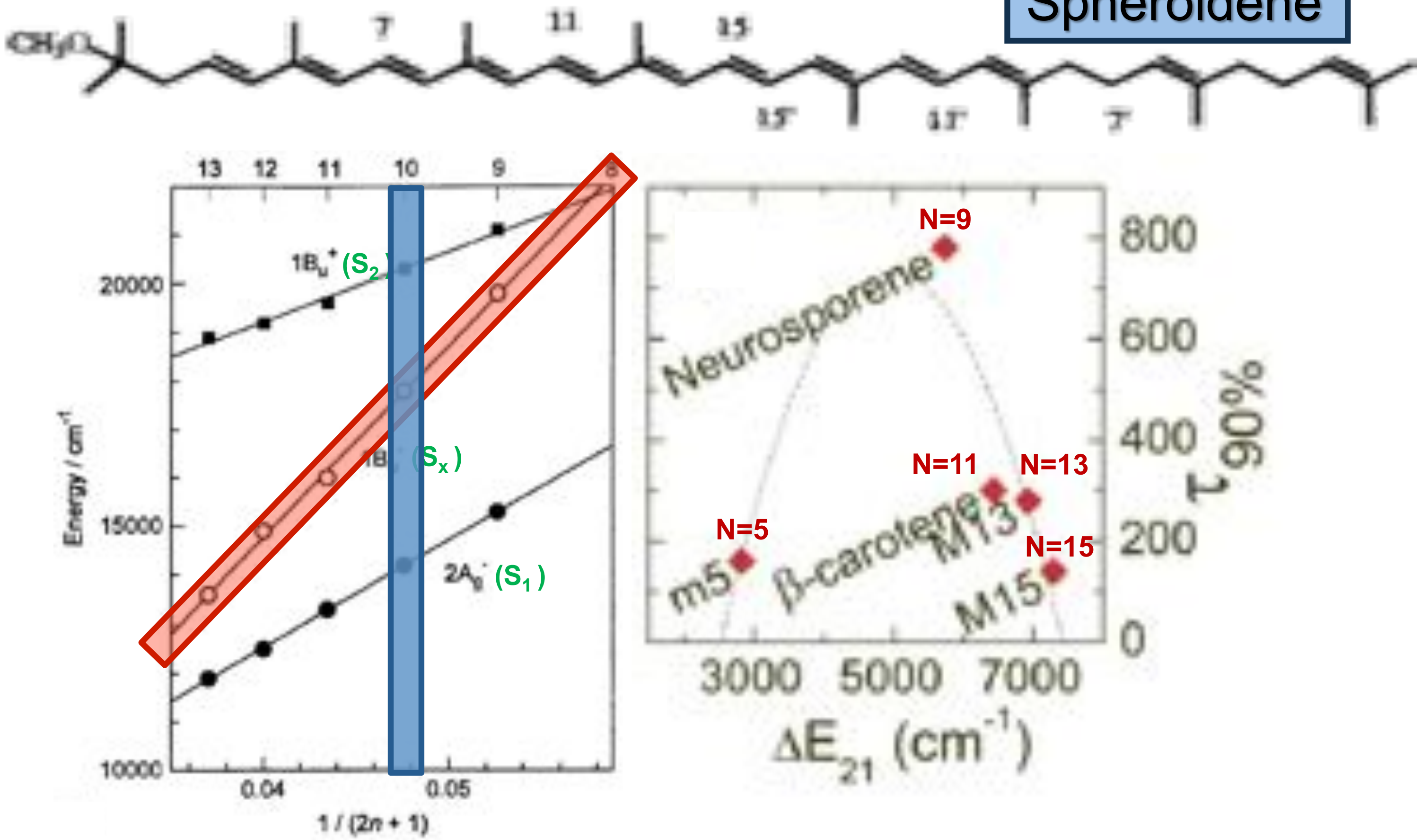
- We extract the **time constants** for the decays

Carotenoid	*n*	k_{2x}^{-1} (fs)	k_{x1}^{-1} (fs)	k_{10}^{-1} (ps)
M_{15}	15	<5	42±4	1.1
M_{13}	13	7±3	105±15	2.8
β-carotene	11	10±2	150±20	4.1
Neurosporene	9	20±5	400±50	20
C_{26}	5	45		2000



Conjugation-length dependence

Spheroidene

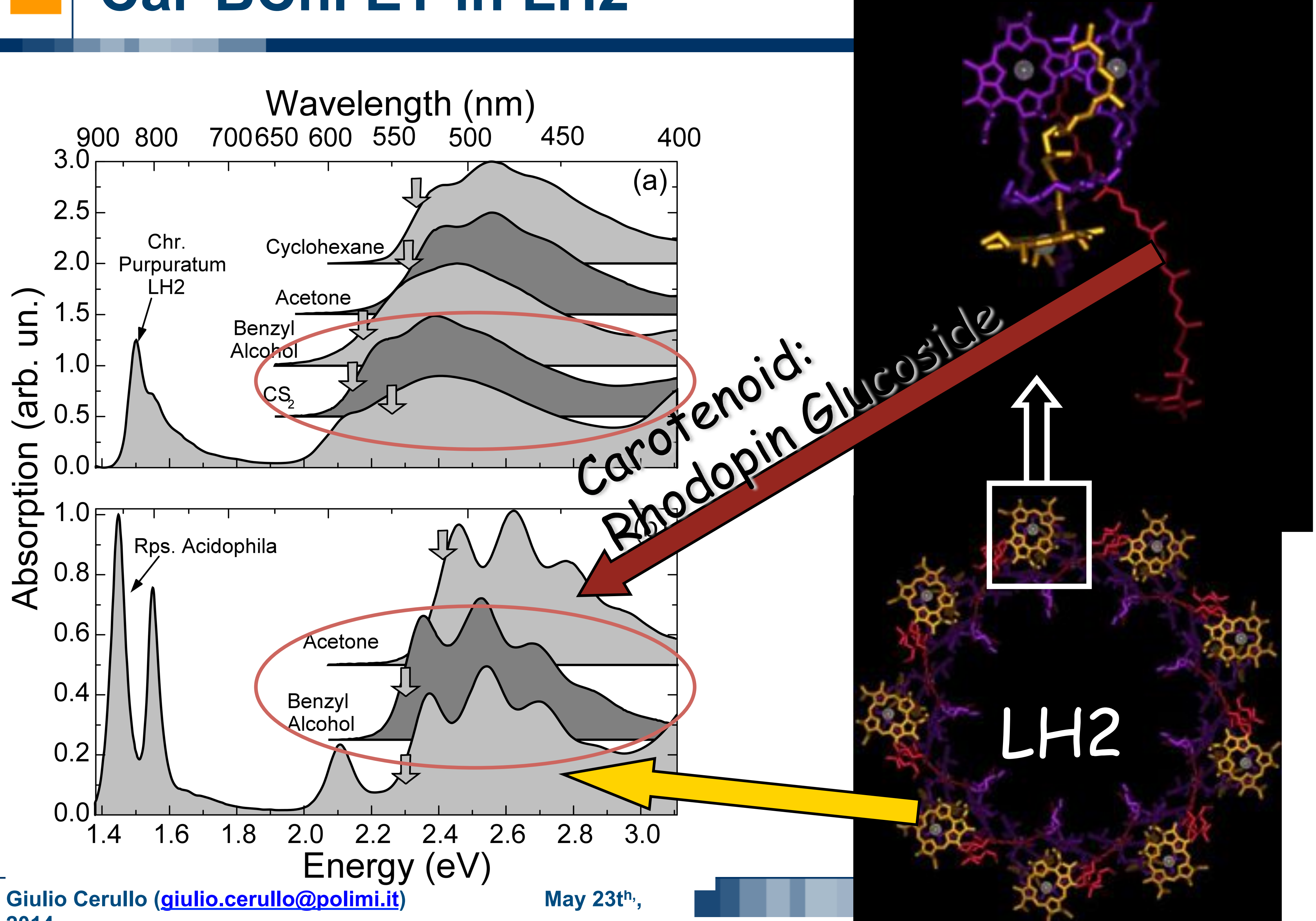


Non-monotonic behavior of $S_2 \rightarrow S_1$ internal conversion

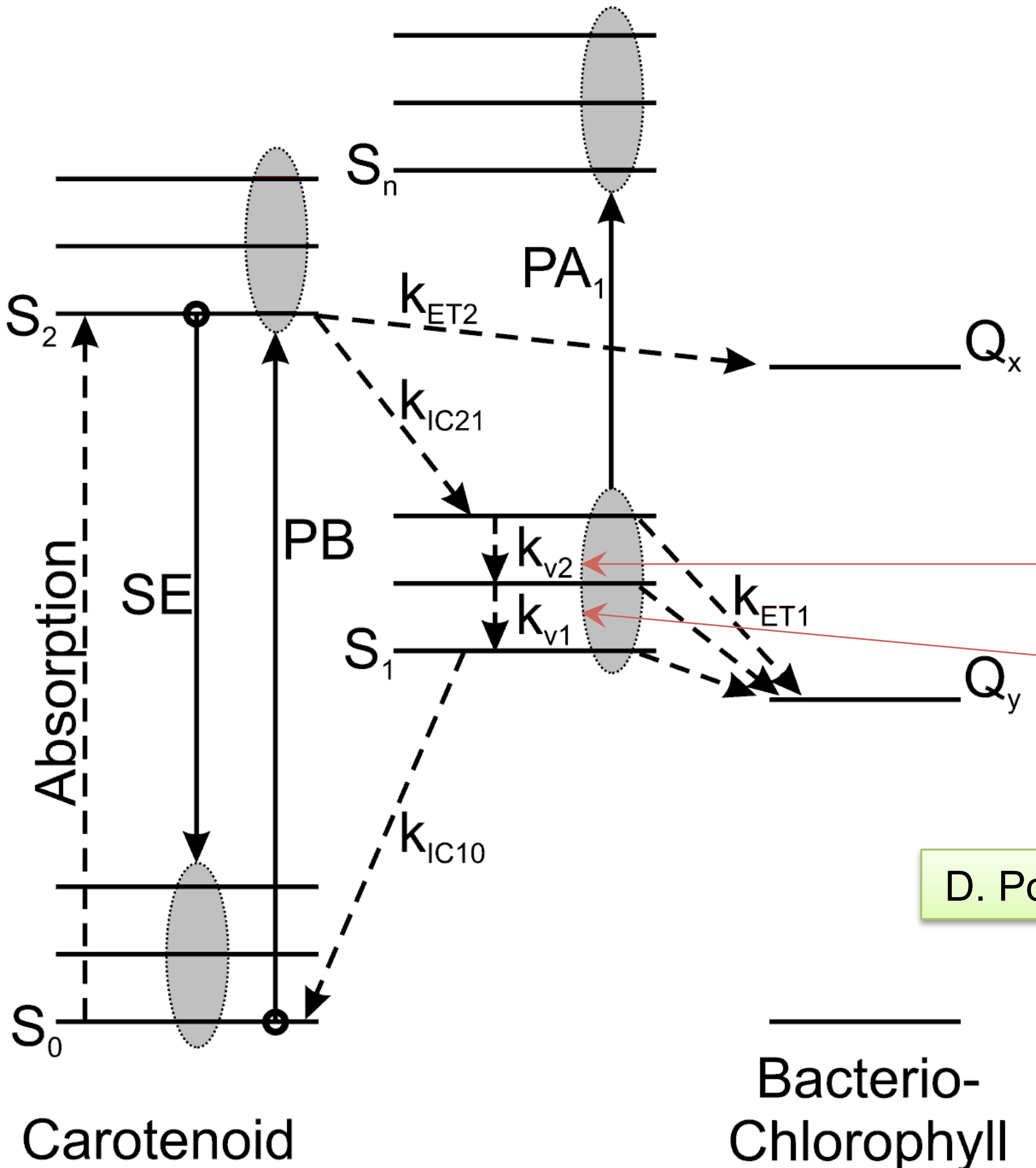
$\Rightarrow$ the intermediate state is involved for carotenoids with n<9!!!

D.Polli *et al., Phys. Rev. Lett* **93**, 163002 (2004)

Car-BChl ET in LH2



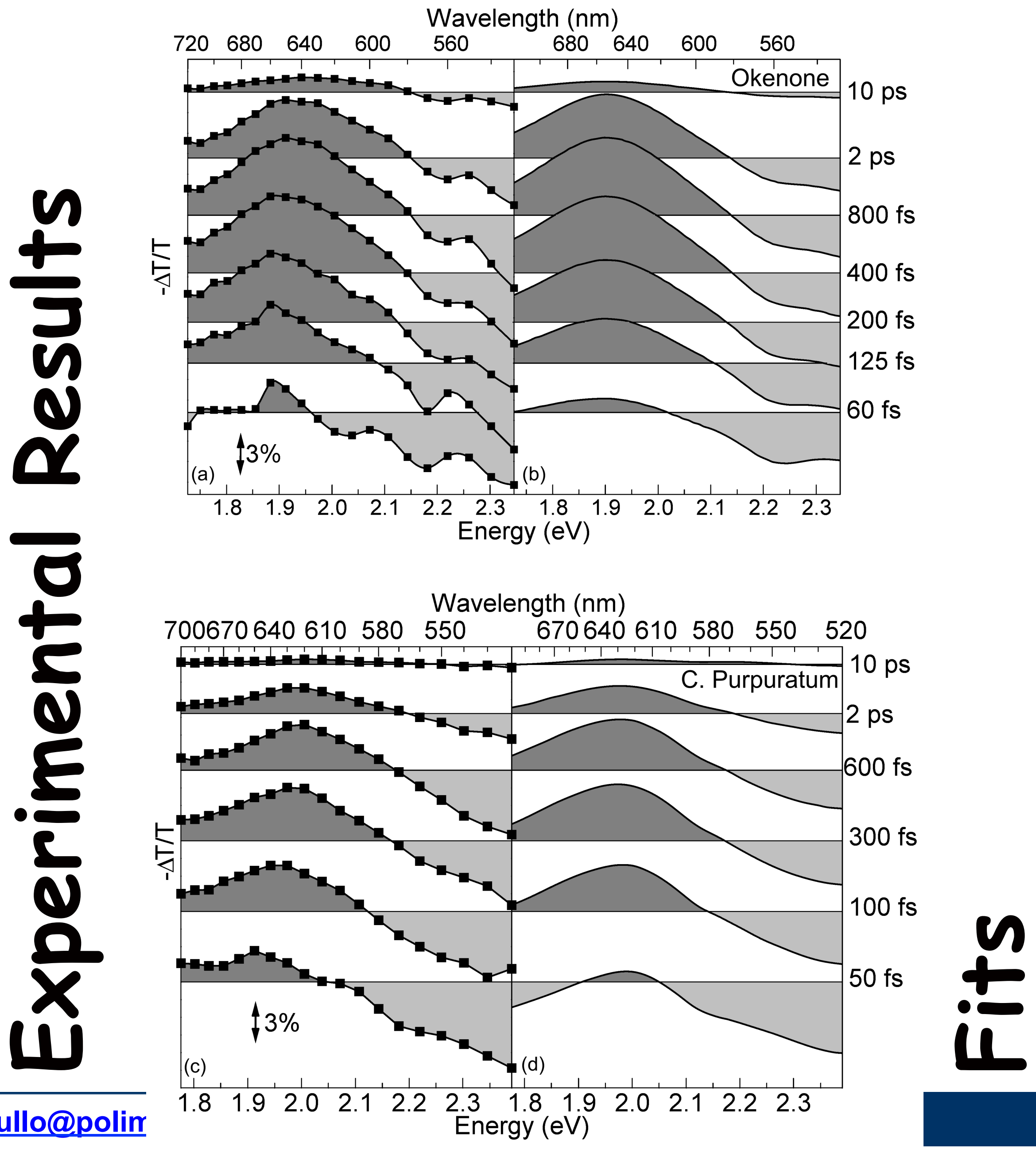
Energy-flow model



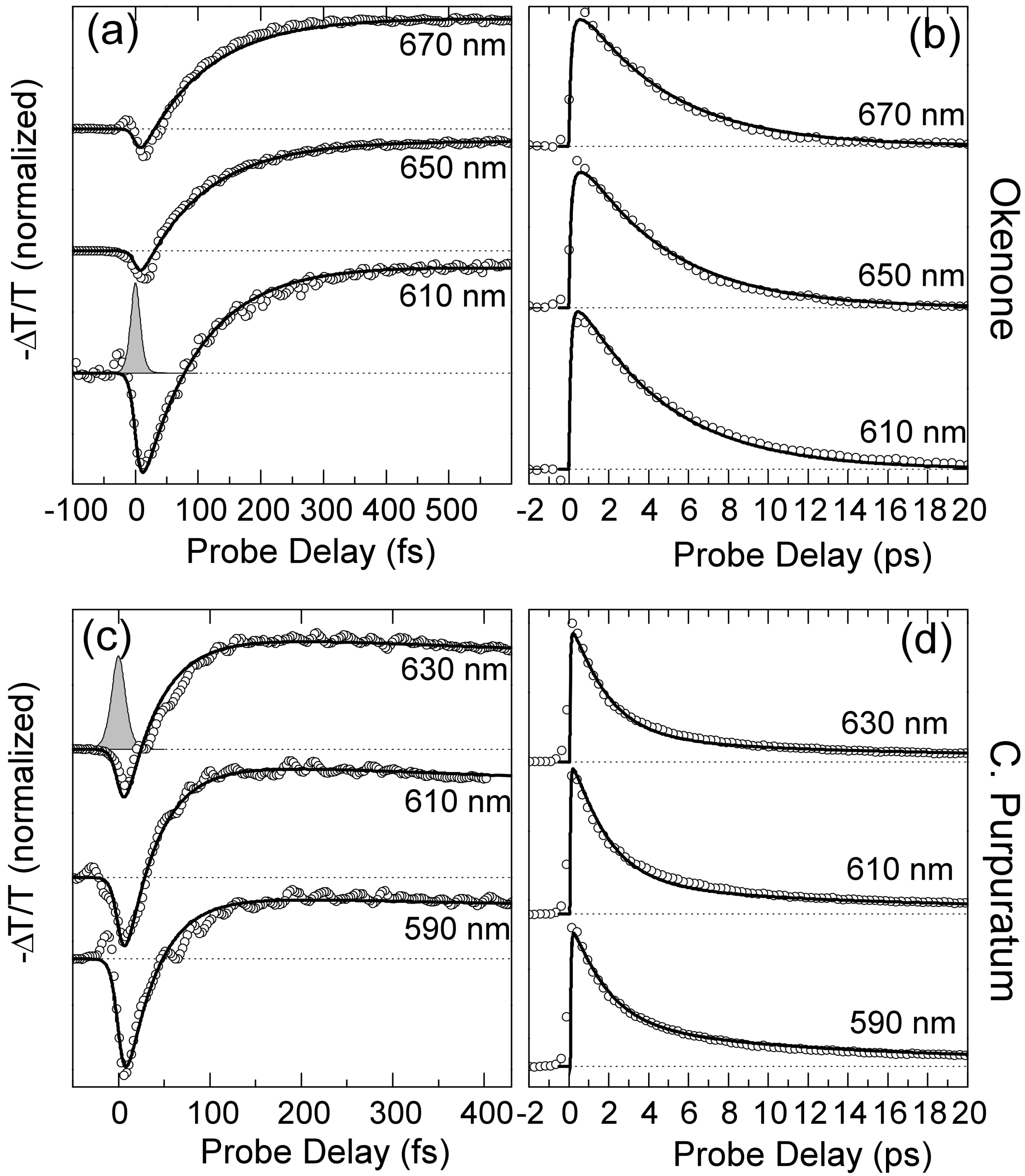
1. **Internal conversion** processes within the excited states in the carotenoids.
2. **Vibrational relaxation** within the excited states.
3. **Energy transfer** from carotenoids to the BChls in the LH2 complexes.

D. Polli et al., Biophys. J. **90**, 2486 (2006)

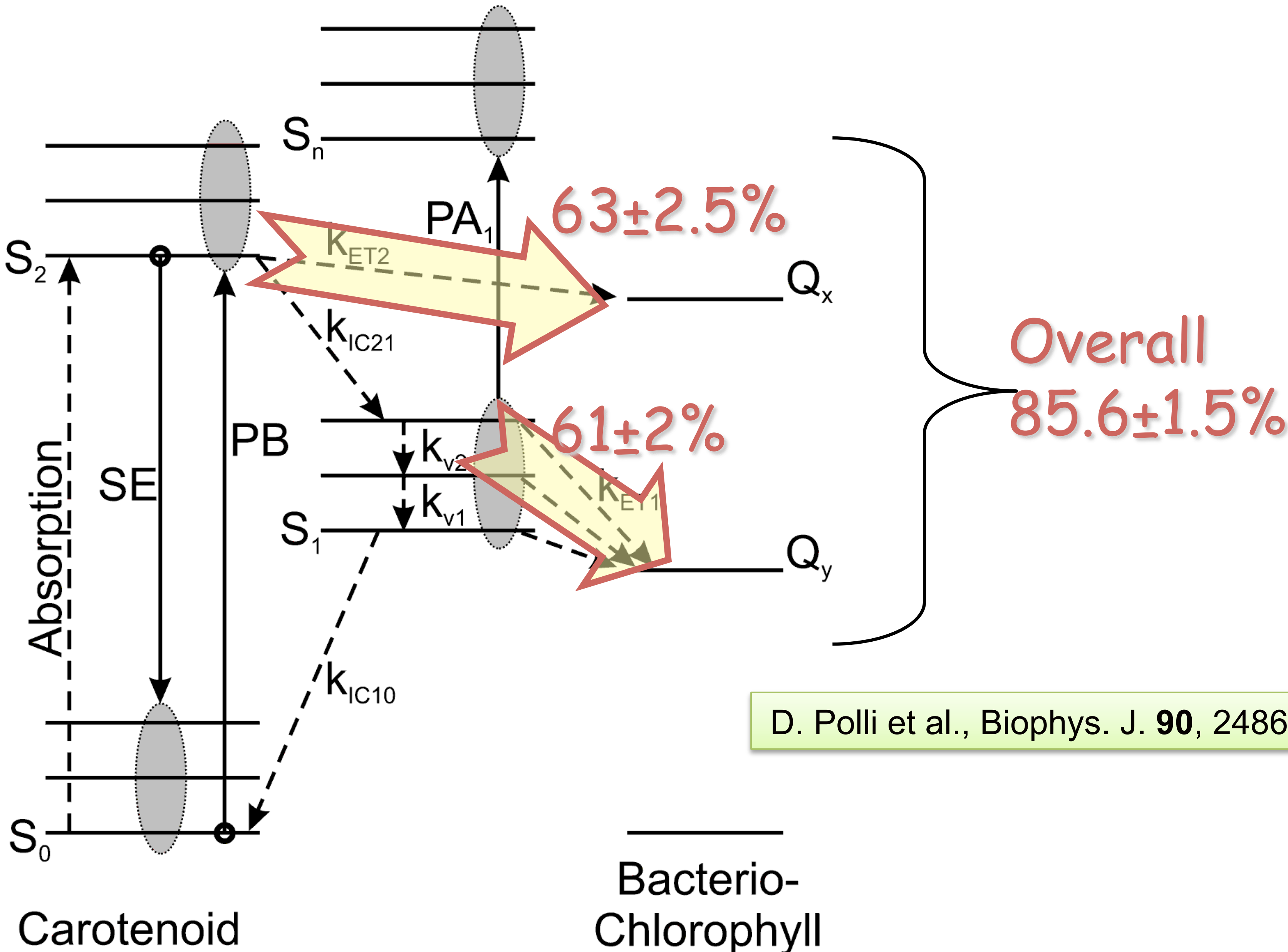
Pump-Probe spectra at various delays



Pump-Probe dynamics at various probe wavelengths

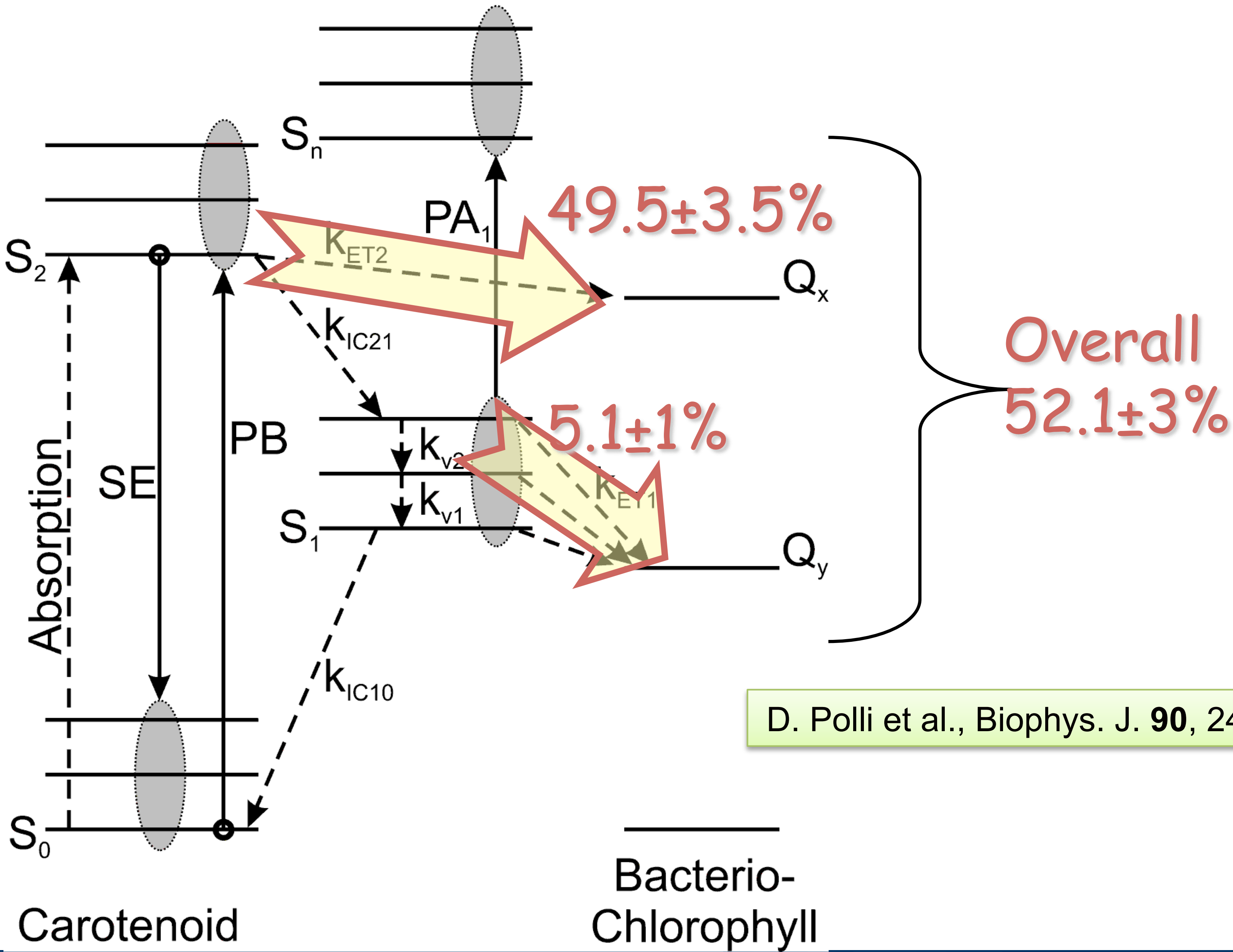


Okenone vs. C. Purpuratum



D. Polli et al., Biophys. J. **90**, 2486 (2006)

Rhodopin Glucoside vs. R. Acidophila

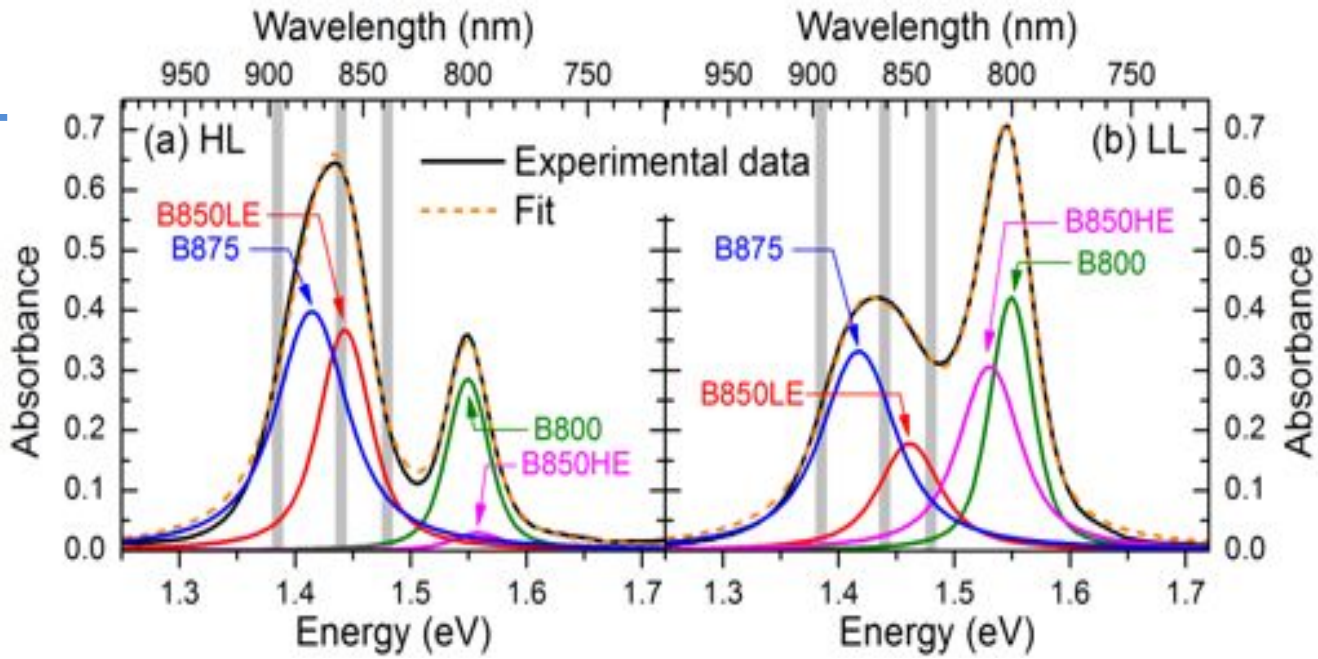


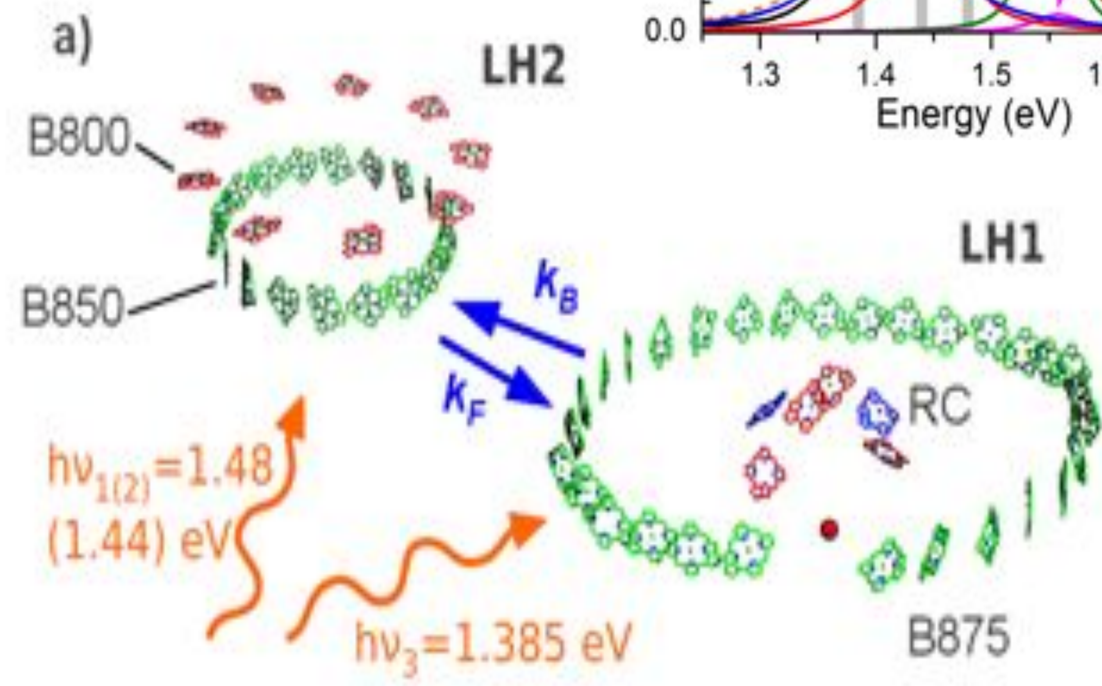
D. Polli et al., Biophys. J. **90**, 2486 (2006)

LH2→LH1 energy transfer

B850 and B875 exciton energies are **close to kT** at room temperature

Energy back transfer B875 → B850 can in principle occur

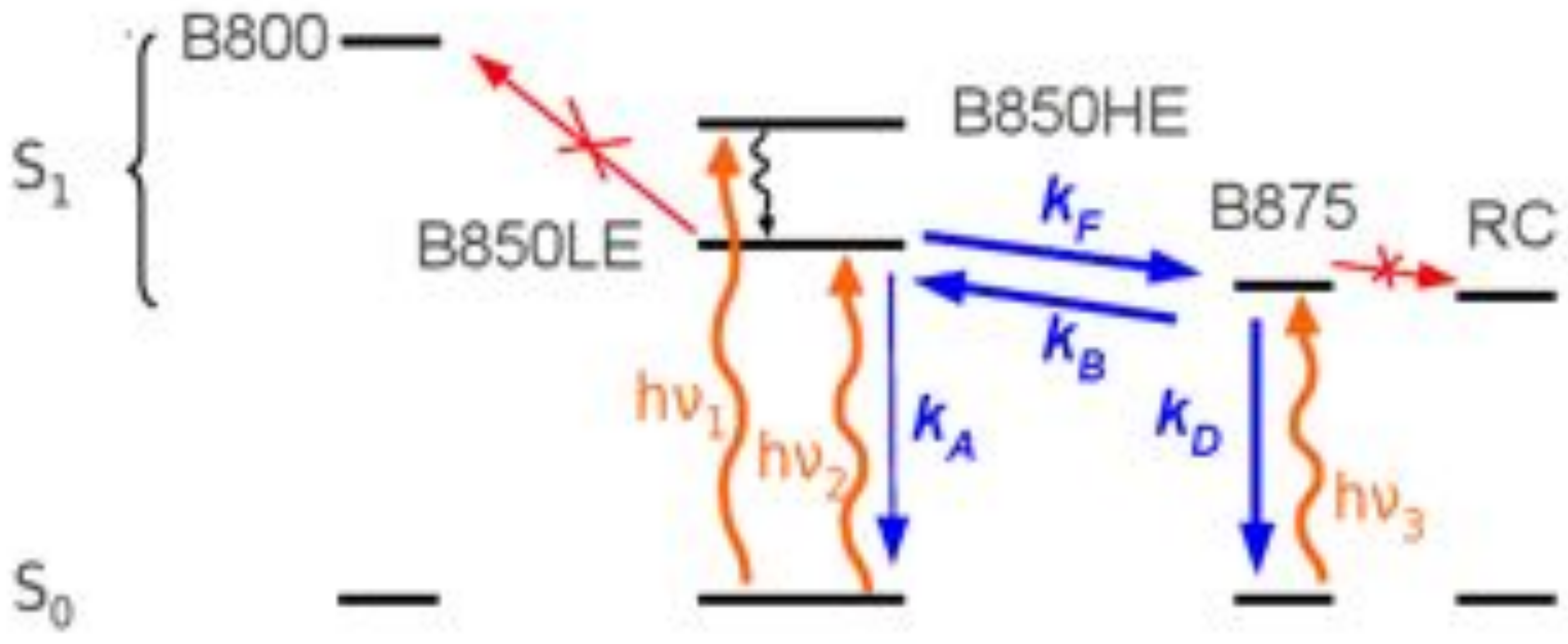




(1) Find out quantitatively if **back transfer** is reduced in LL

(2) Explain the **selective advantage** for the bacteria to do so

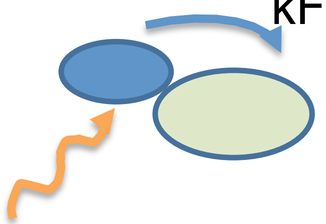
Equilibration and equilibrium



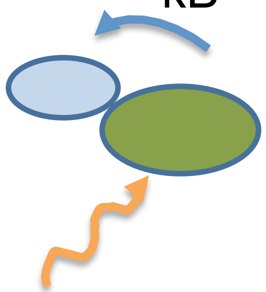
- Reaction scheme leading to an **equilibrium**
- Direct time domain measurement of **forward and back transfer**
- Problem: Kinetics will always yield a combination of k_F and k_B. Need to measure the **equilibration kinetics** AND the **equilibrium**!

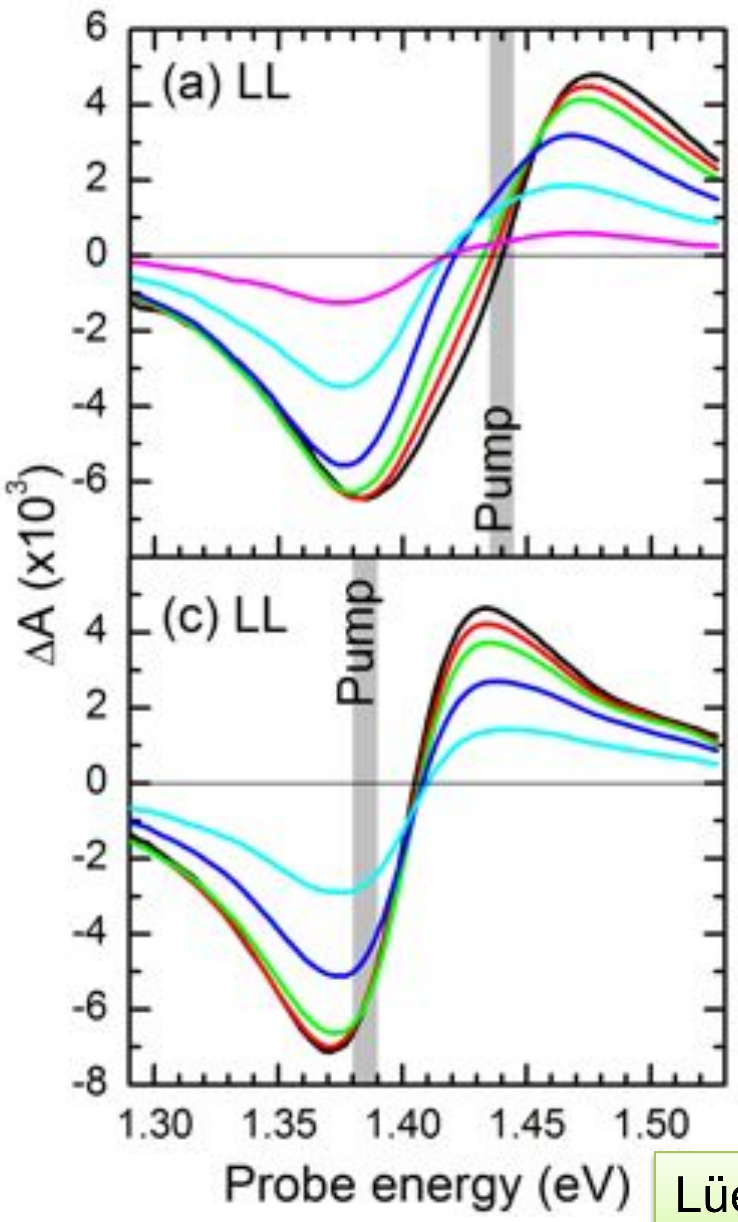
Transient absorption spectra in LL

E(pu)= 1.44 eV
(predominant-
ly B850)



E(pu) = 1.38 eV
(predominantly
B875)



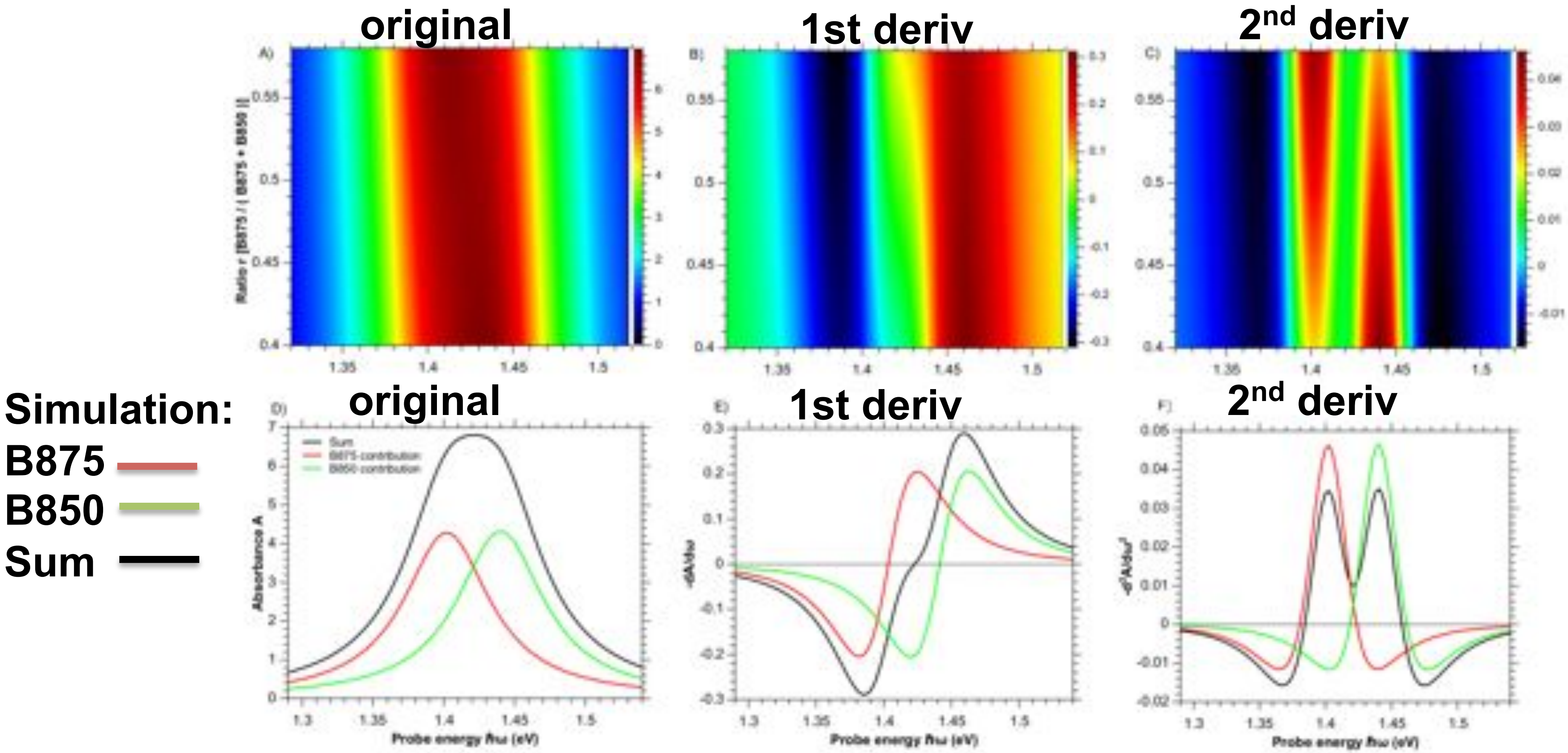


TA spectra look like **first derivatives** of the ground state absorption spectra.

Information on energy transfer somehow in the **red or blue shift** of the x axis intersection

Lüer *et al., PNAS* **109**, 1473 (2012)

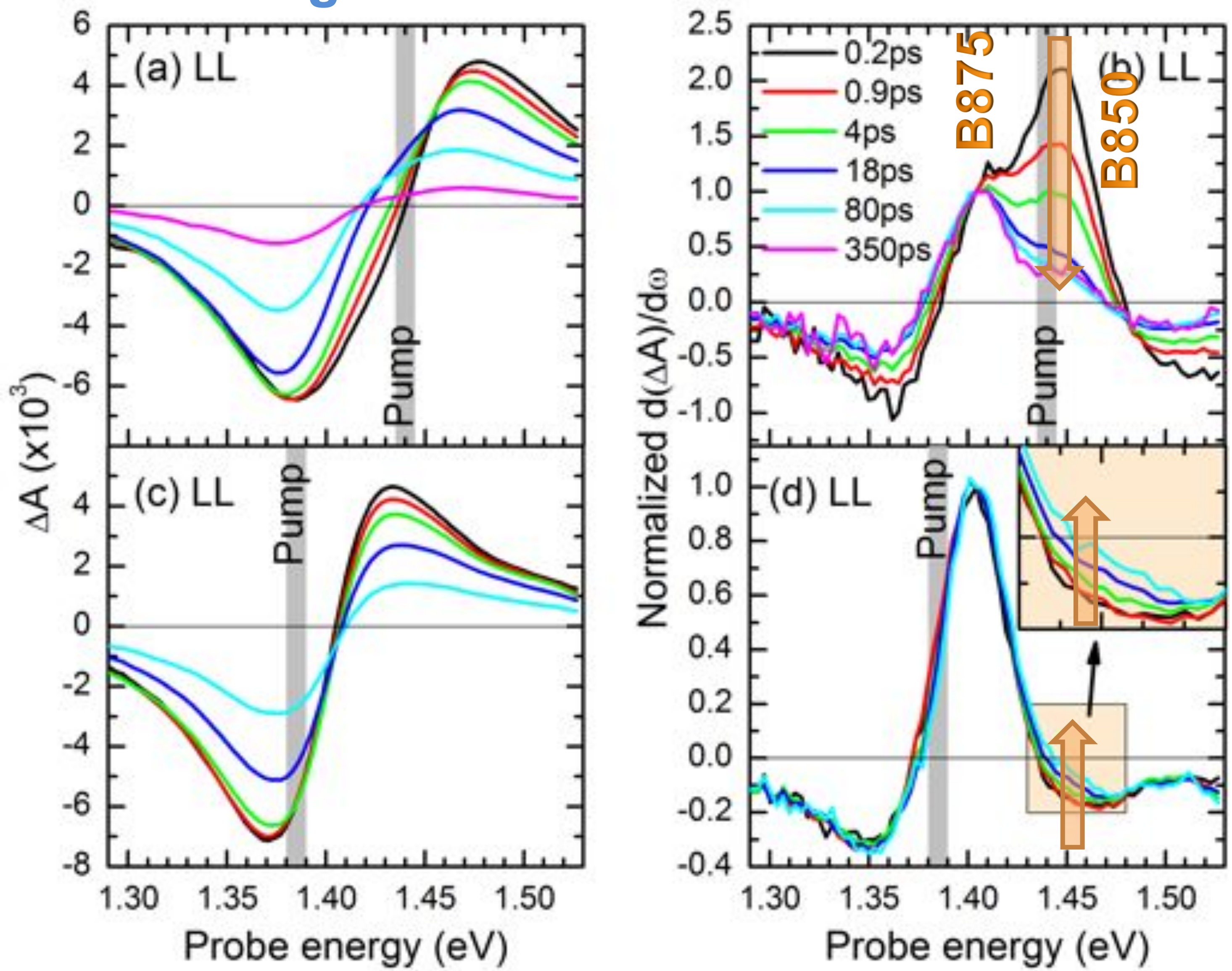
Derivative spectroscopy



- 2nd derivative of any symmetric peak function has a peak at same position as original function, but much **smaller bandwidths**
- PP spectrum is already first derivative of GA spectrum
- 1st derivative of PP spectrum should look like 2nd derivative of GA spectrum

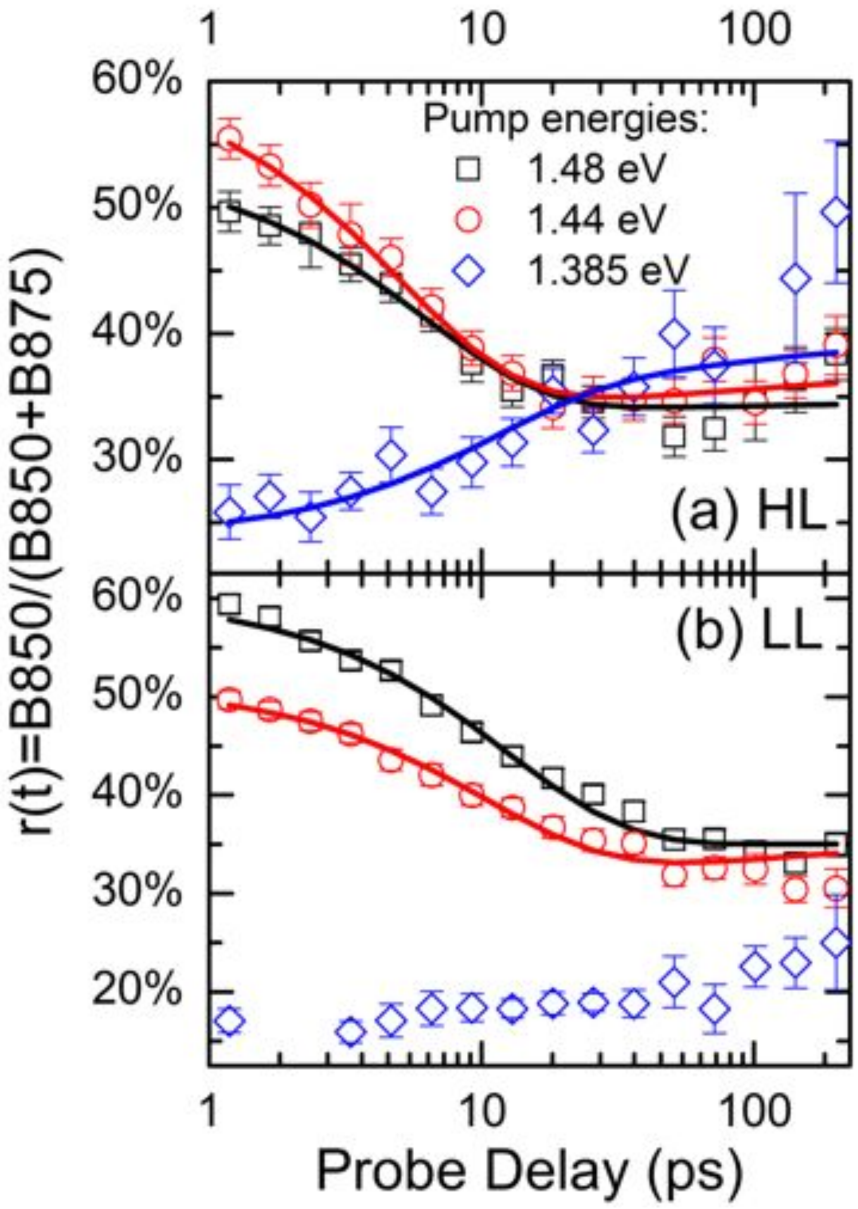
First derivatives of TA spectra

original | 1st derivative



- Time-dependent B850↔B875 amplitudes ⇒ **equilibration**!
- Constant B850/B875 ratio for t >50 ps ⇒ **equilibrium**!
- Final derivative spectra depend on **pump photon energy**

ET rate constants



- **Low-light adaptation**: reduced elementary backward ET rate, because lower probability of two simultaneous excitations reaching the same LH1/RC complex under weak illumination.

- **Backward ET** is not just an inevitable consequence of vectorial ET with small energetic offsets, but is in fact **actively managed** by photosynthetic bacteria.

Lüer *et al., PNAS* **109**, 1473 (2012)

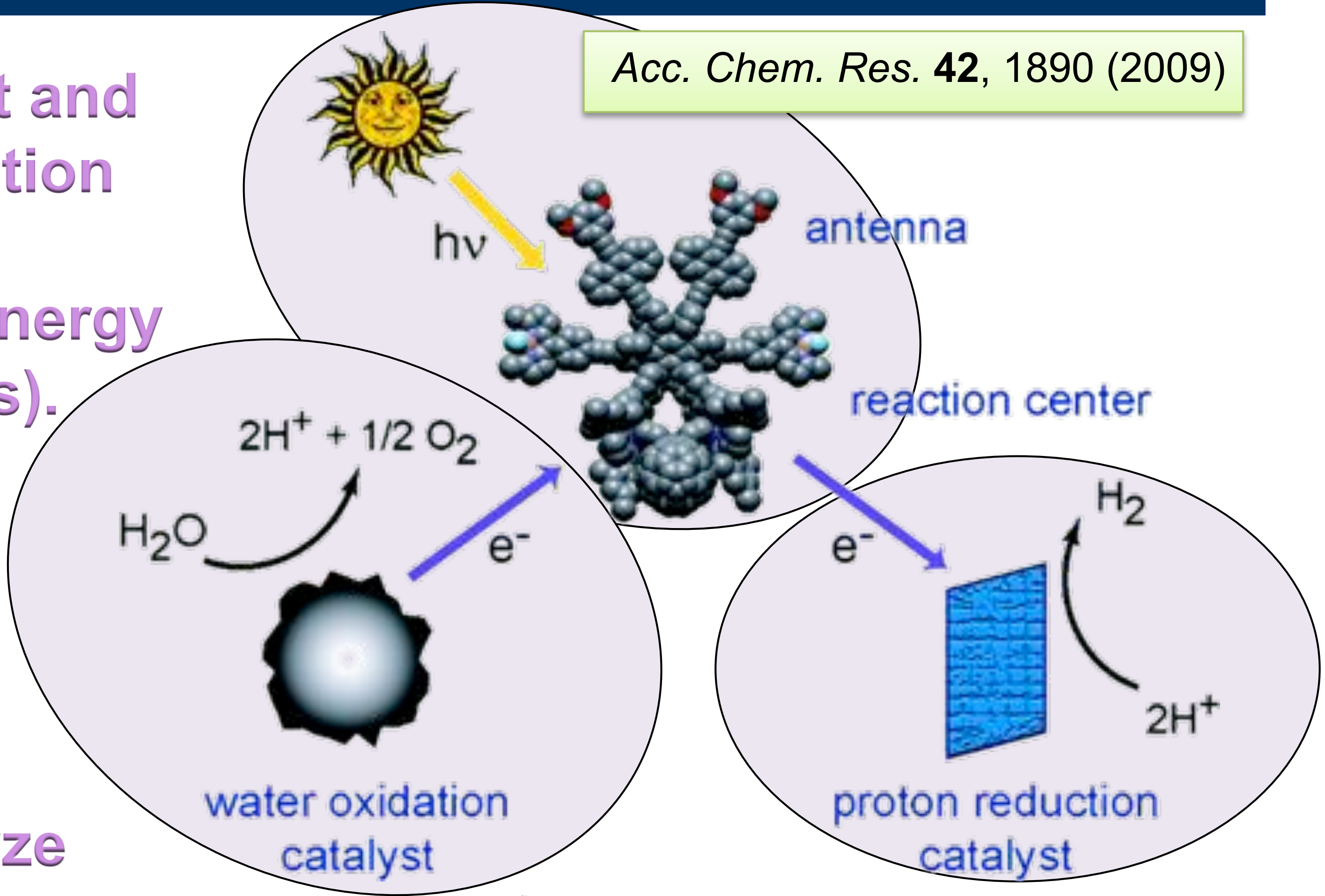
Outlook

1. Photosynthetic Light Harvesting
2. Ultrafast spectroscopy
3. Natural Light-Harvesting complexes: purple bacteria
4. Artificial Light-Harvesting complexes: dyads and triads
5. Organic photovoltaic (OPV) devices: bulk heterojunctions

Artificial photosynthesis

1) absorb sunlight and convert the excitation energy to electrochemical energy (redox equivalents).

Acc. Chem. Res. **42**, 1890 (2009)



2) use this redox potential to catalyze conversion of water to hydrogen ions, electrons stored as reducing equivalents, and oxygen.

3) use the the reducing equivalents to make fuels such as carbohydrates, lipids, or hydrogen gas.

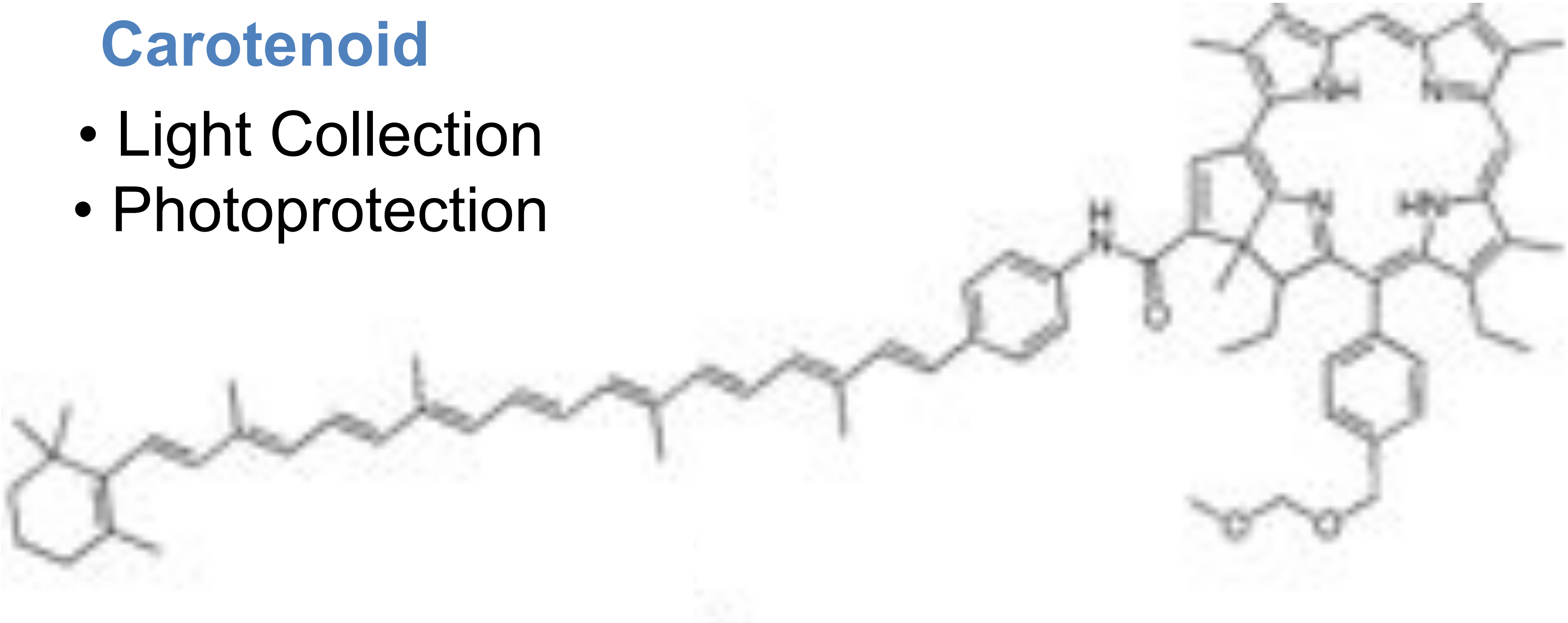
Supramolecular dyads

Phtalocyanine/ Porphyrines

•Energy Acceptor

Carotenoid

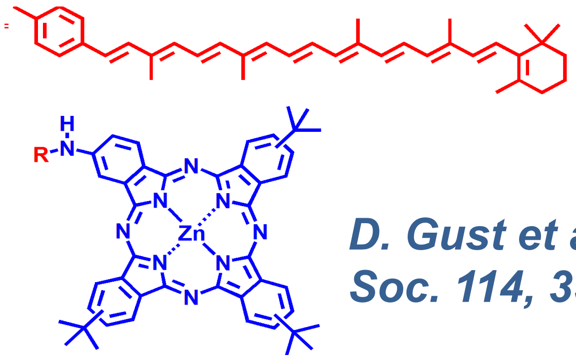
- Light Collection
- Photoprotection



Artificial light -harvesting supramolecular systems

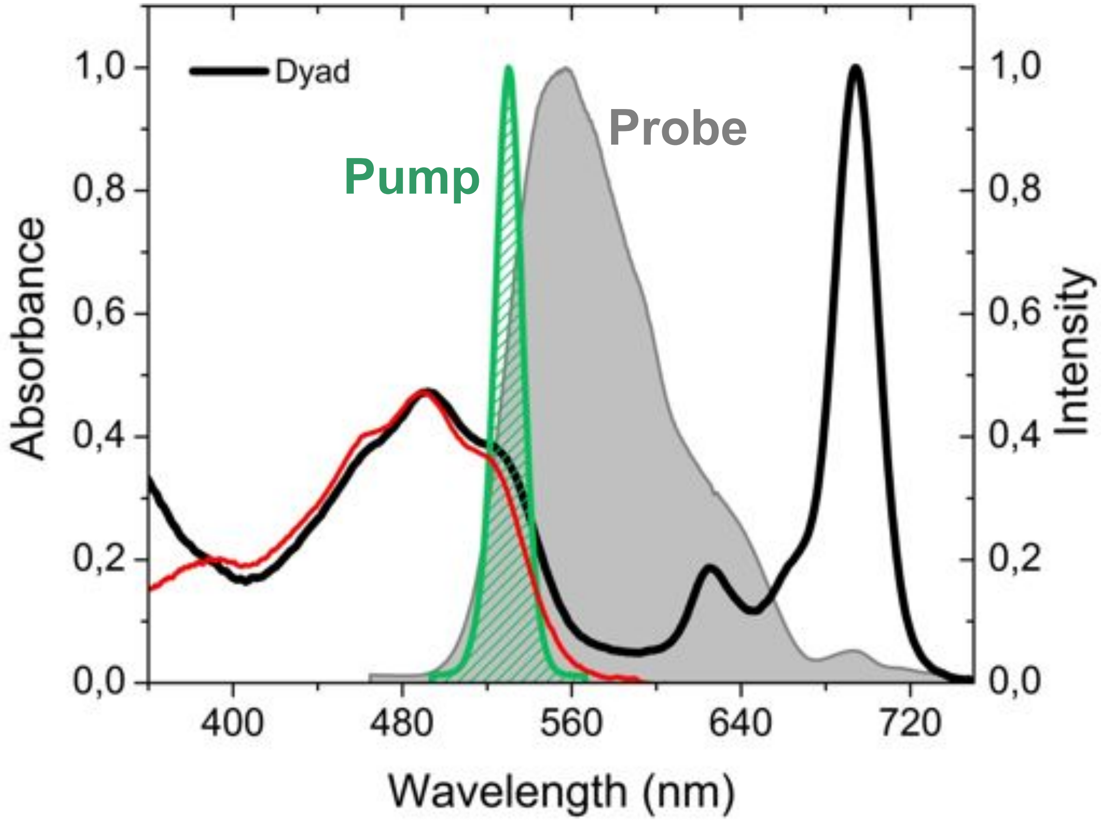
The System

- Artificial System: **PC-Car-**



D. Gust et al., J. Am. Ch
Soc. 114, 3590 (1992)

M. Kloz et al., J. Am. Ch
Soc., 133, 7007 (2011).

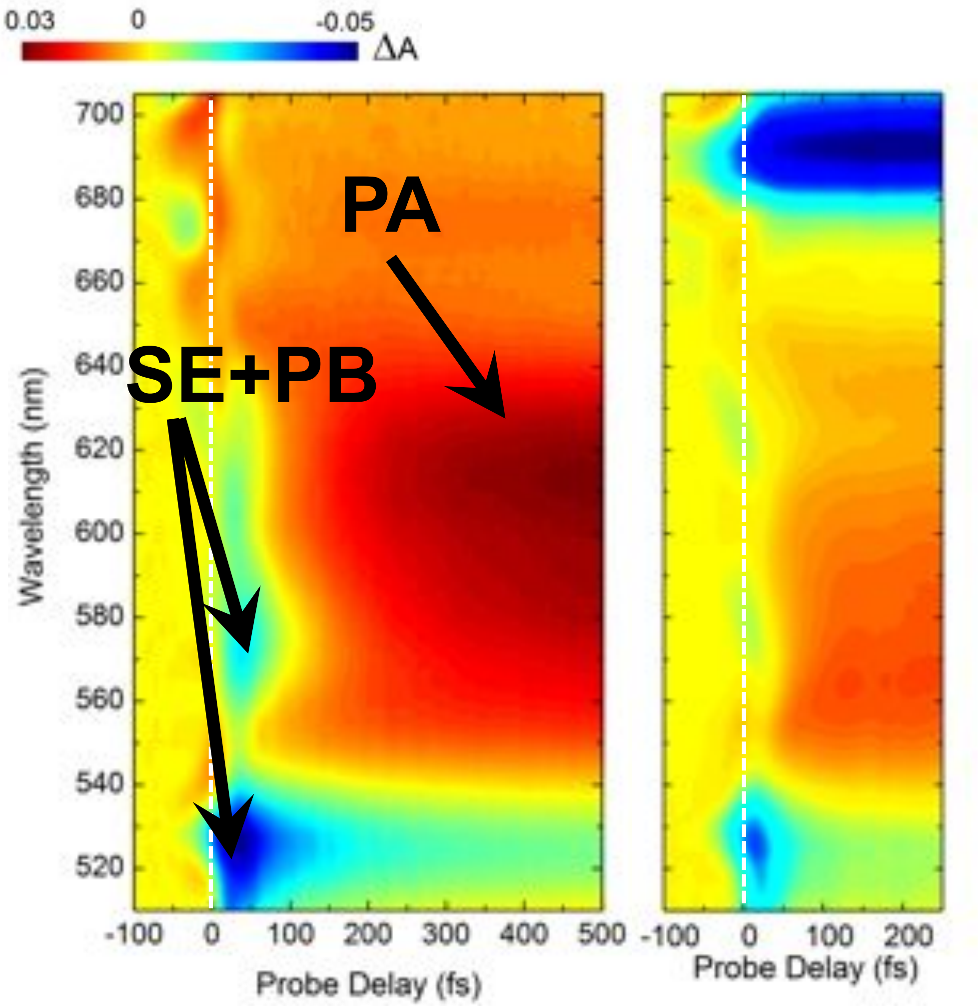


The Goal

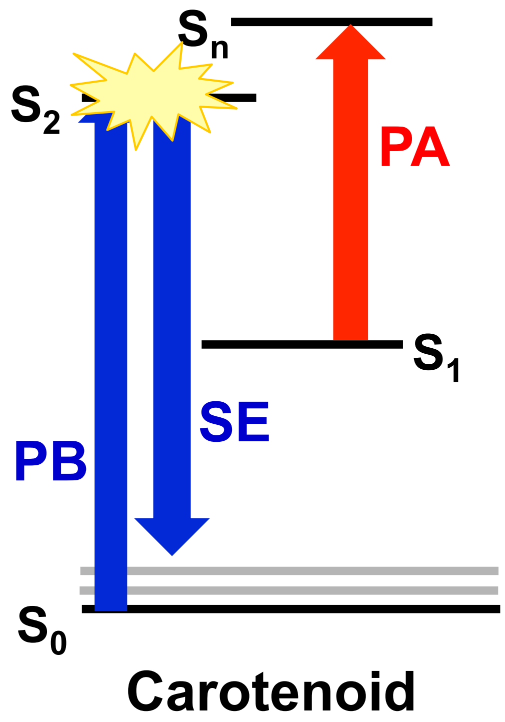
- Understand energy branching pathways

Exciting the Carotenoid

2D Pump-Probe maps :

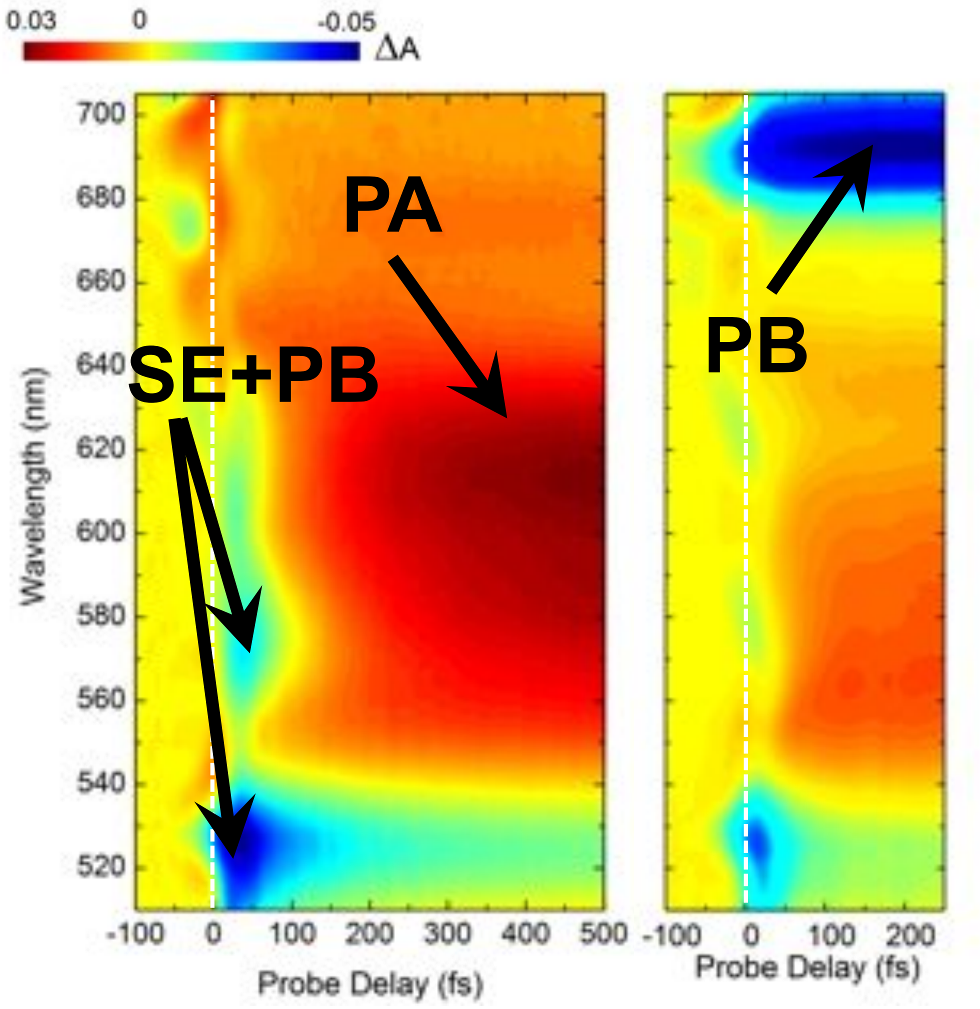


Carotenoid **Dyad**

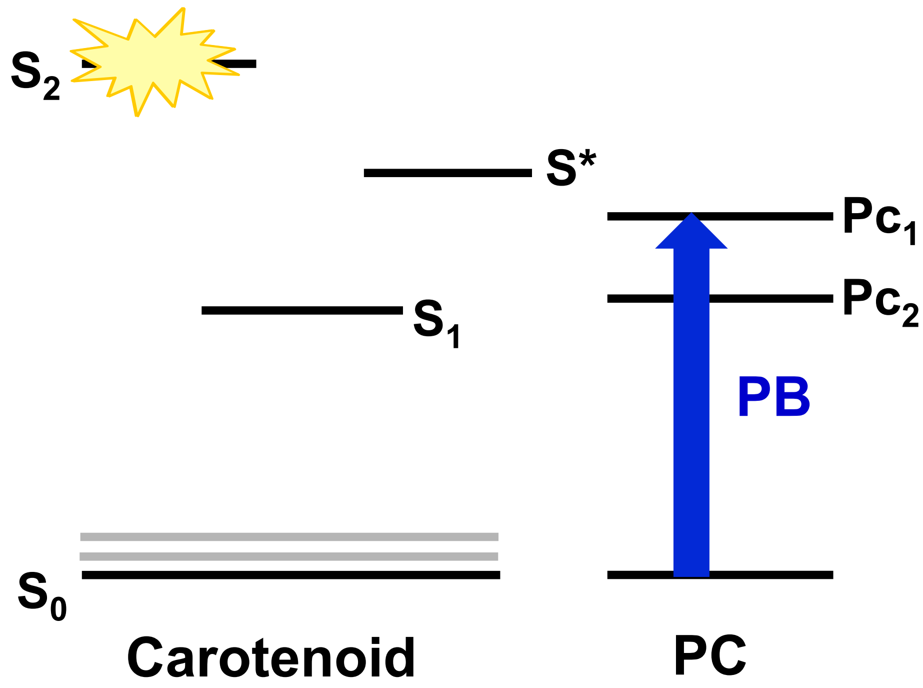


Exciting the Carotenoid

2D Pump-Probe maps :

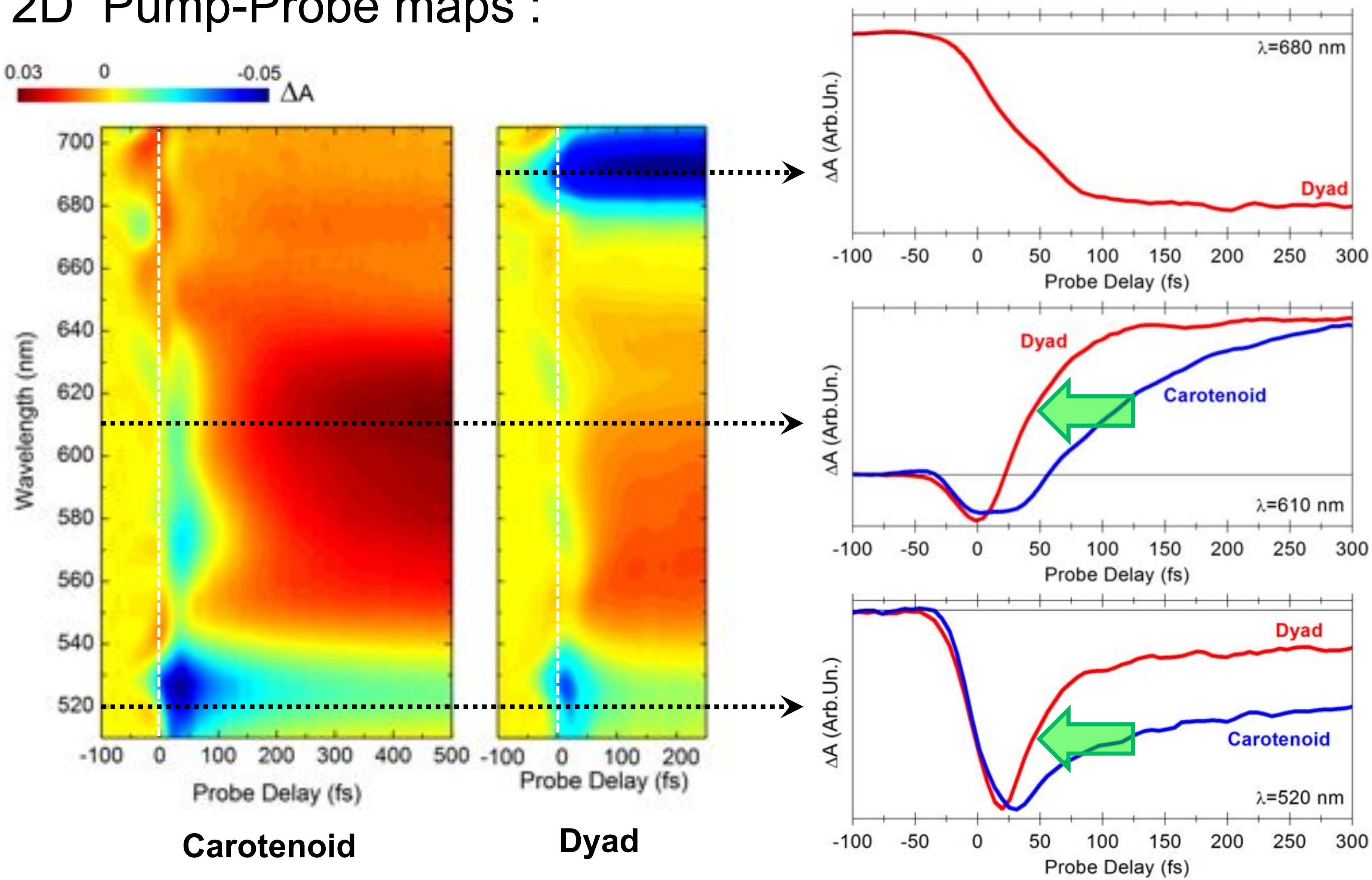


Carotenoid Dyad



2D Pump-Probe maps :

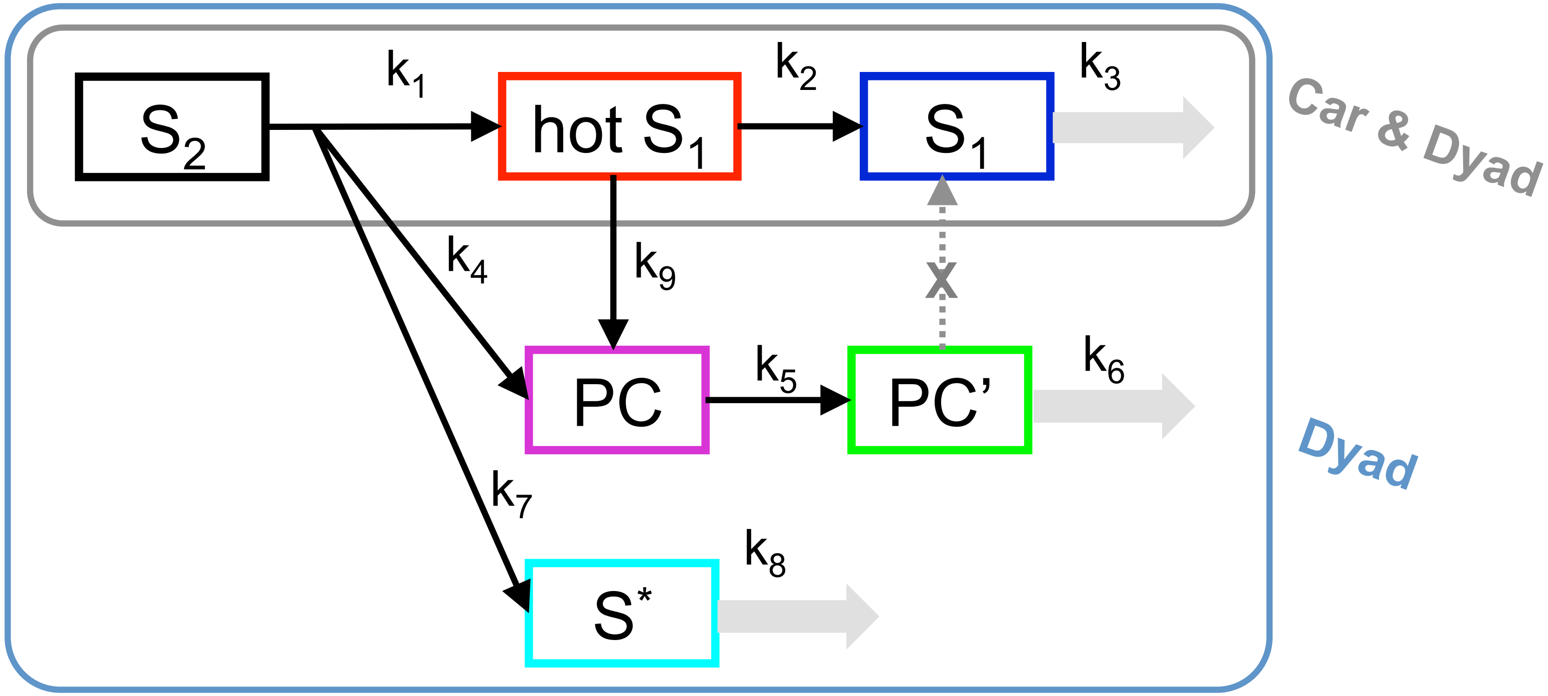
temporal traces



Global and Target Analysis

All data at all wavelengths and all time points are analyzed *simultaneously :*

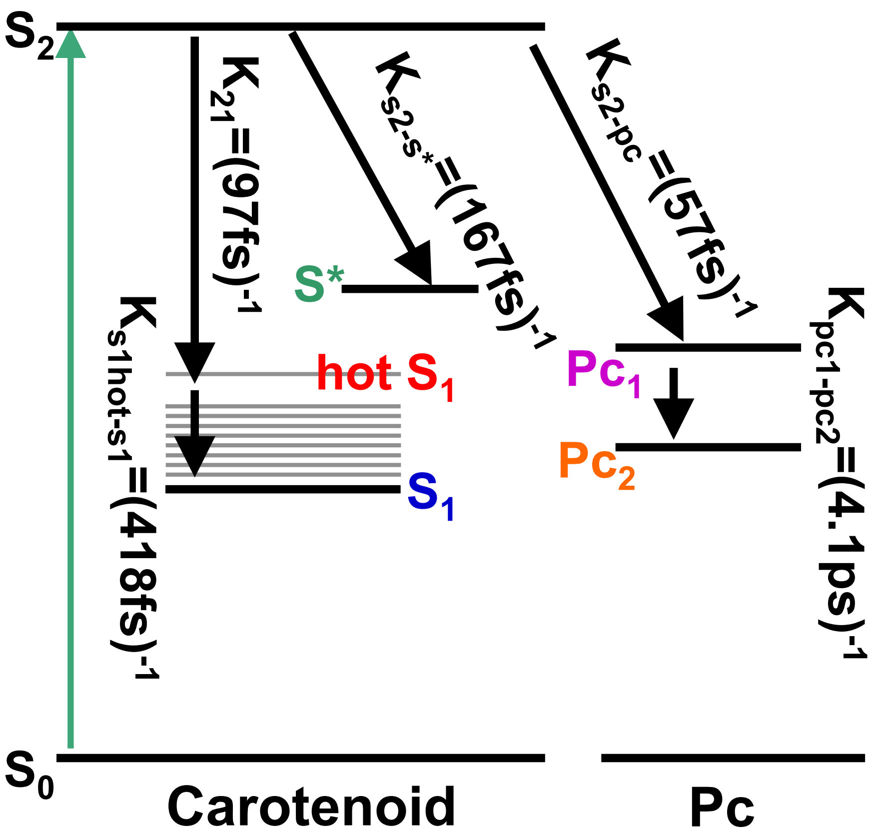
- description of the kinetics of the isolated Car and Dyad
- compartmental model

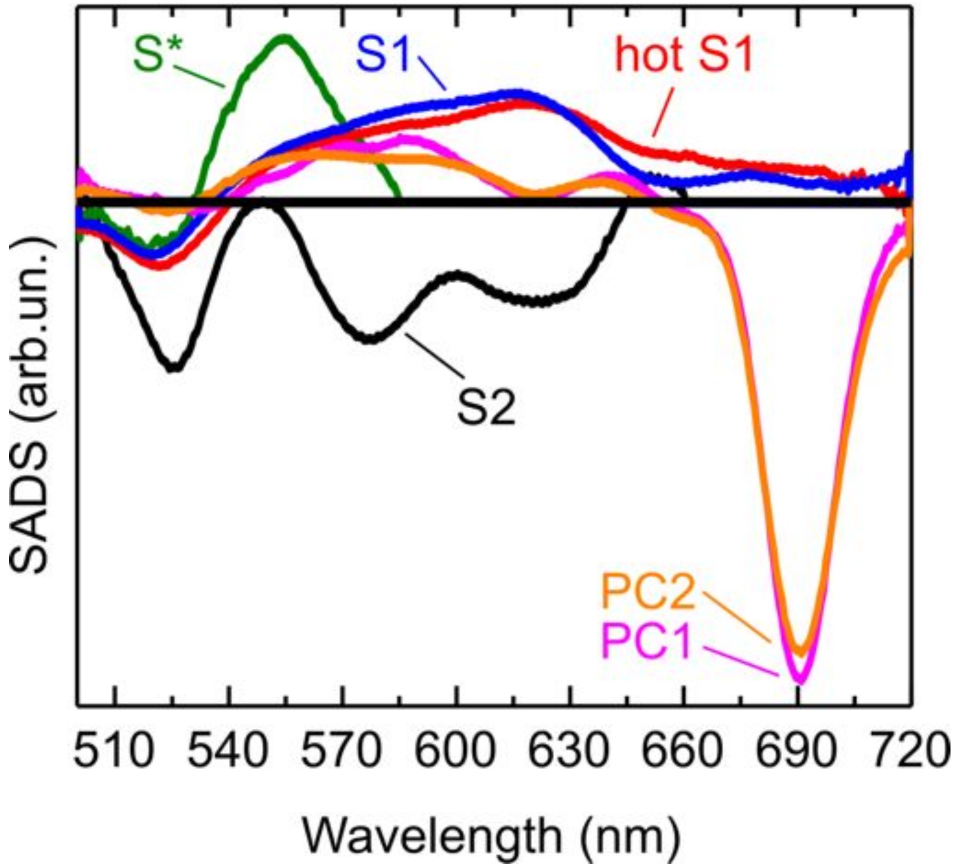


I. H. M. van Stokkum, D. S. Larsen, and R. van Grondelle, "Global and target analysis of time resolved spectra," Biochimica Et Biophysica Acta,1657, (2004).

Global and Target Analysis

Extracted rate constant :



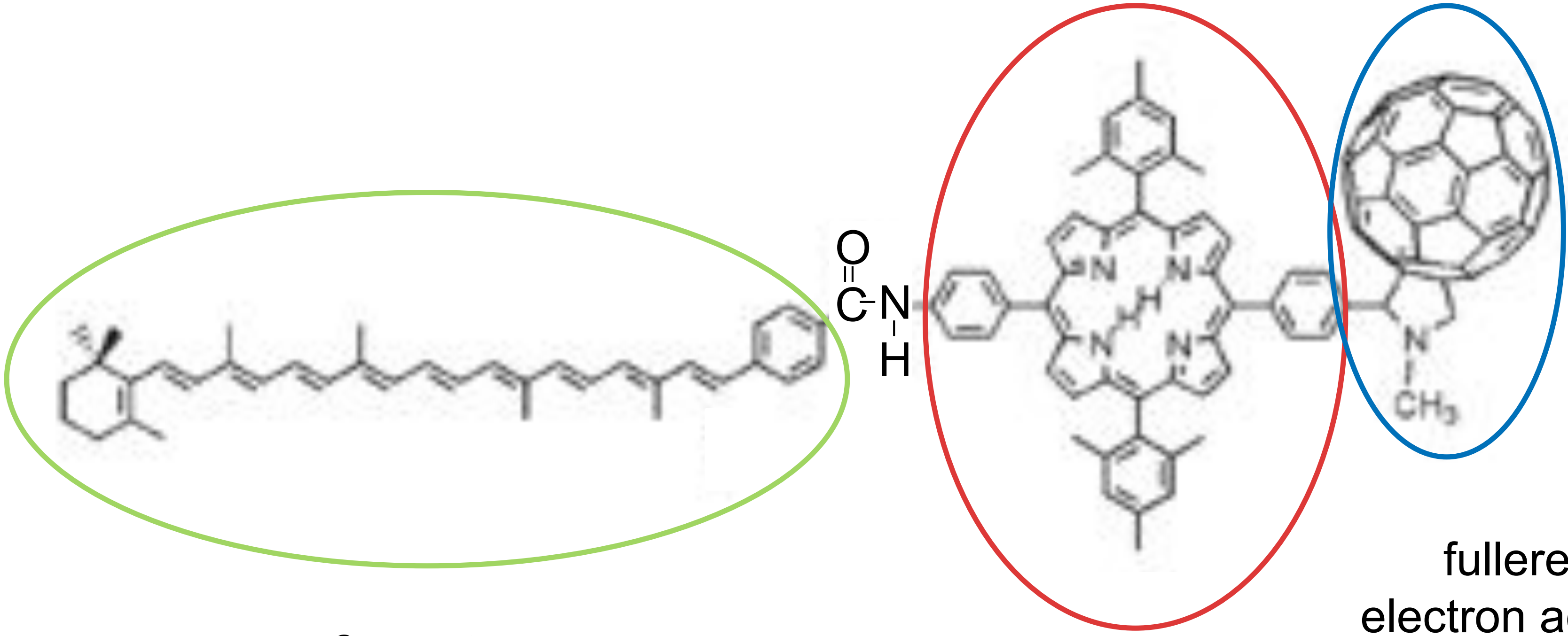


$$\eta_{ET} = \frac{k_{S_2-PC}}{k_{S_2-S*} + k_{S_2-S_1} + k_{S_2-PC}}$$

Energy Transfer Efficiency ≈52%

A supramolecular triad

An artificial model system mimicking solar energy conversion



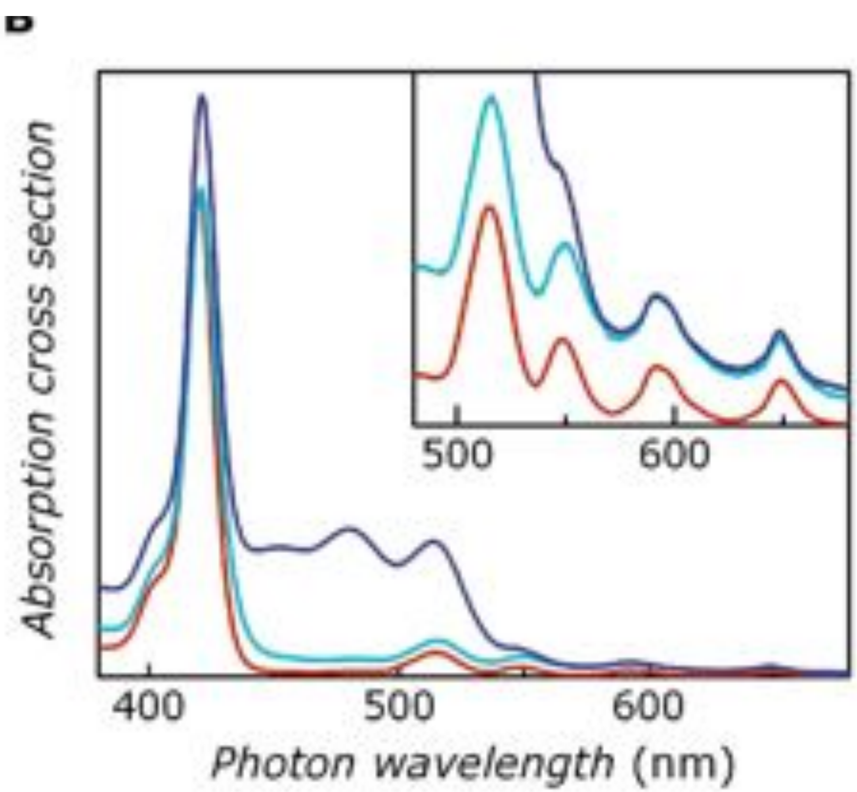
β-carotene:
hole stabilization
(hole acceptor)

porphyrin:
light absorption

fullerene:
electron acceptor

…mimics photosynthetic reaction center

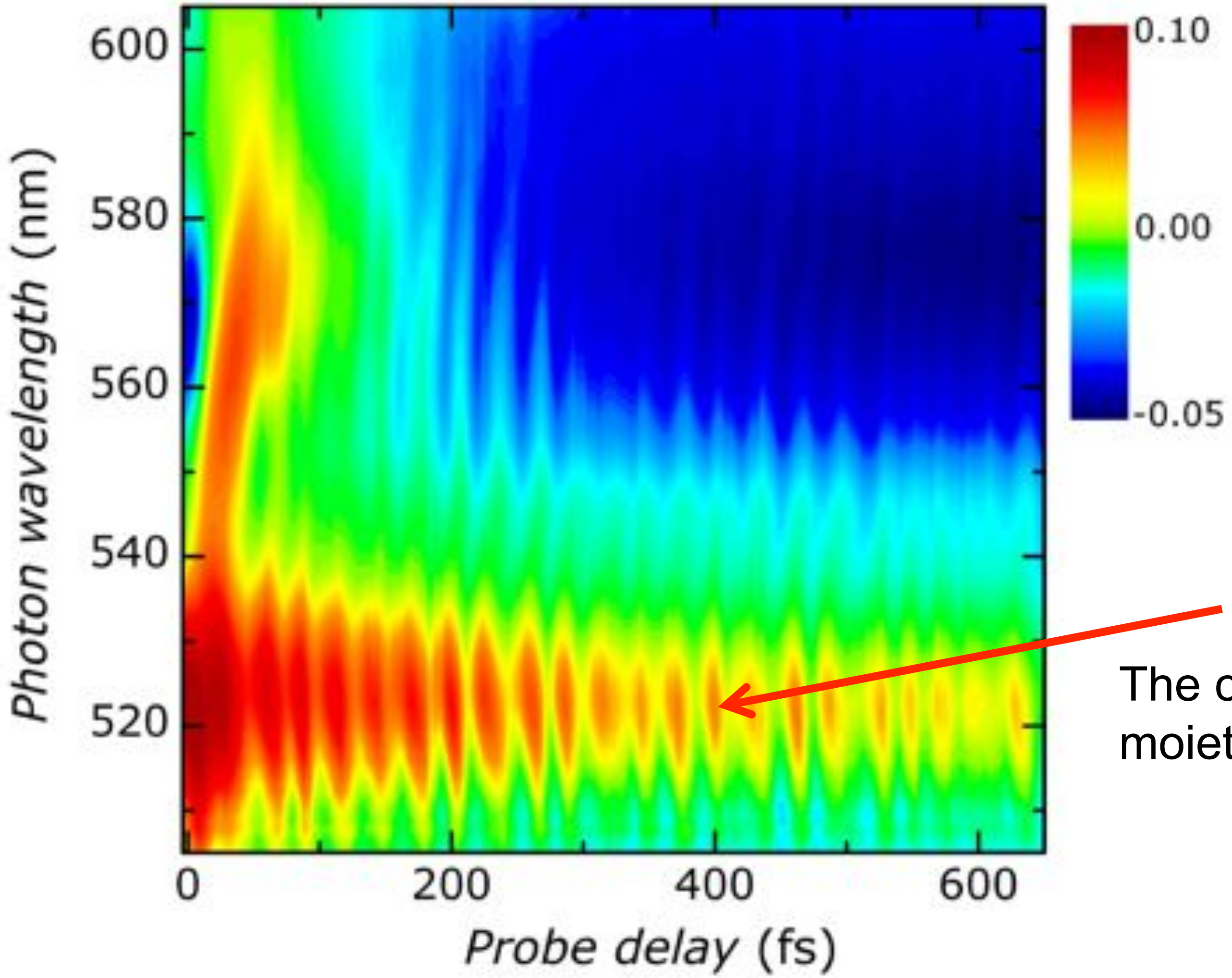
Triad absorption spectra



— Triad
— Porphyrin-Fullerene Diad
— Porphyrin
— Carotene

s. also G. Kodis et al, J. Phys. Org. Chem. 17, 724 (2004).

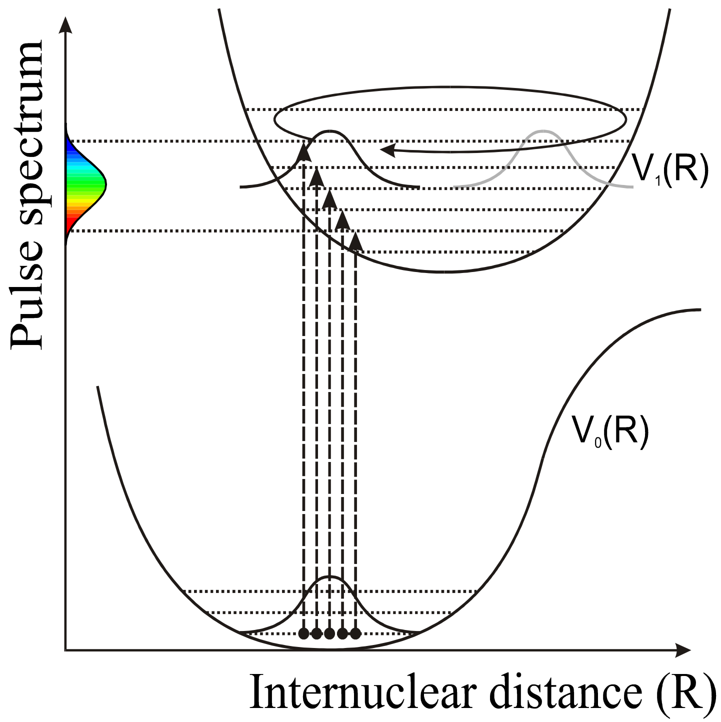
Pump-Probe Trace of Triad (Excitation on the porphyrin)



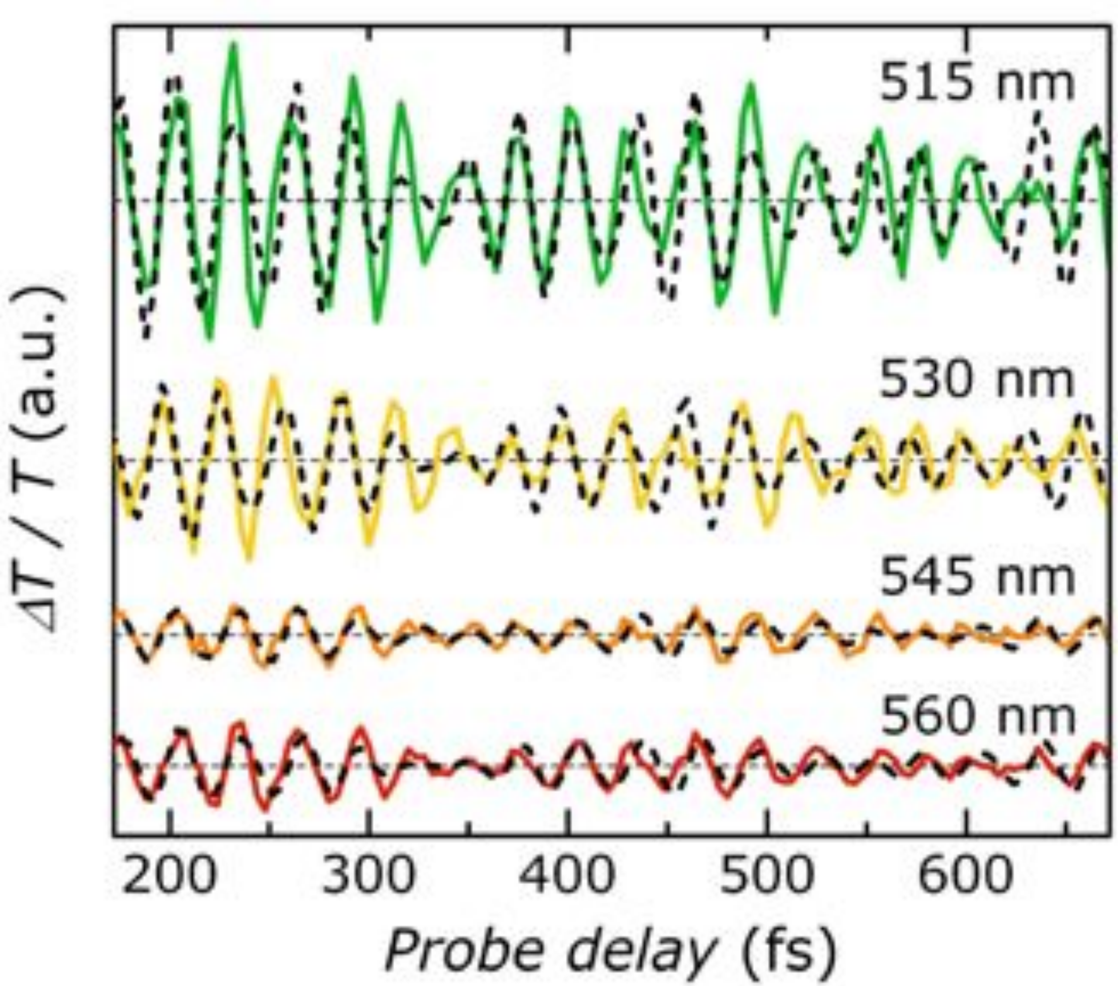
The carotene moiety oscillates

Impulsive Vibrational Spectroscopy

- **Time-domain description:** excitation without nuclear motion, due to short pulsewidth ⇒ molecule oscillates around non-equilibrium position in the excited state.
- **Eigenstate description:** the short pulse excites in phase many vibrational eigenstates ⇒ a wavepacket is formed on the excited state potential energy surface.



Analysis of the β-carotene oscillations

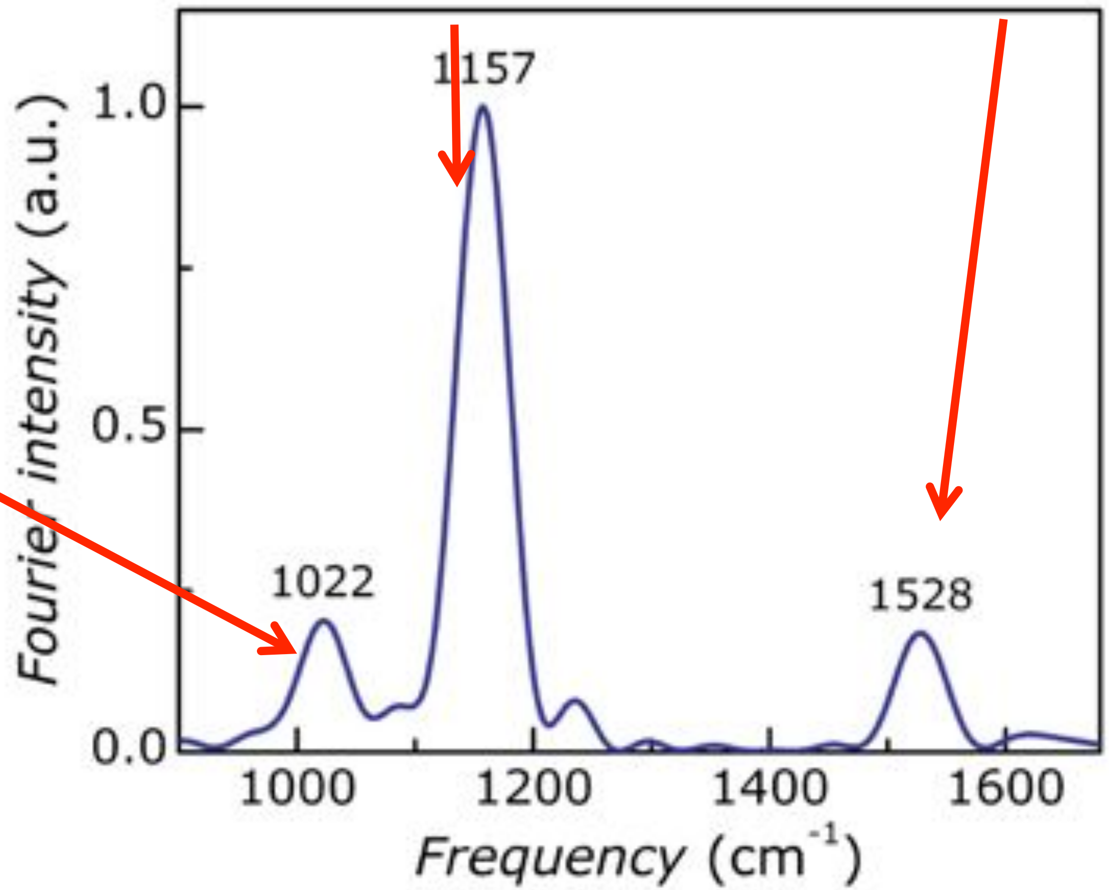


Analysis of the β-carotene oscillations

C-C stretch
(1155 cm^{-1})

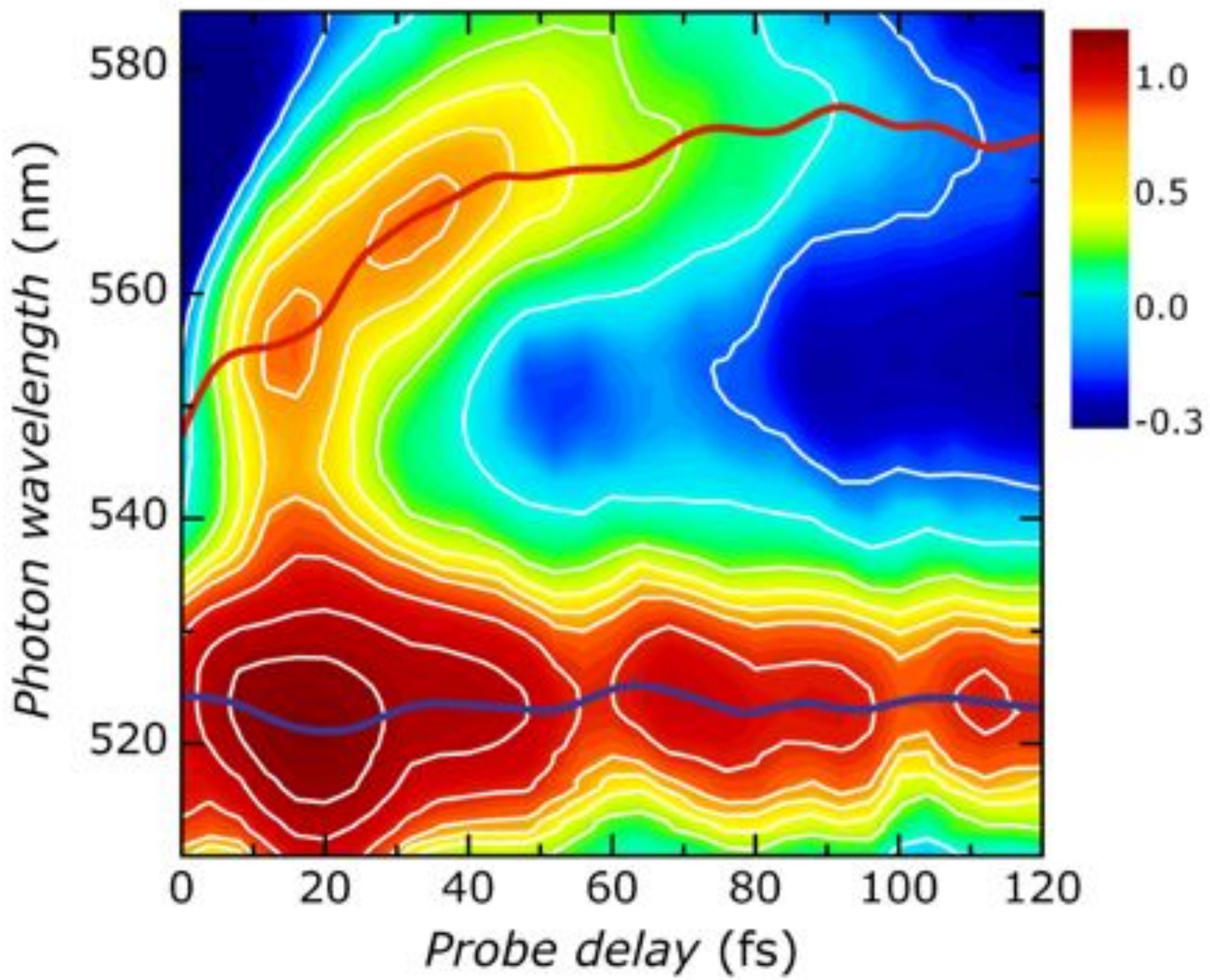
C=C stretch
(1523 cm^{-1})

Methyl rocking
mode
(1003 cm^{-1})



Now that we understand the β-carotene oscillations …
… we can safely remove them from the data

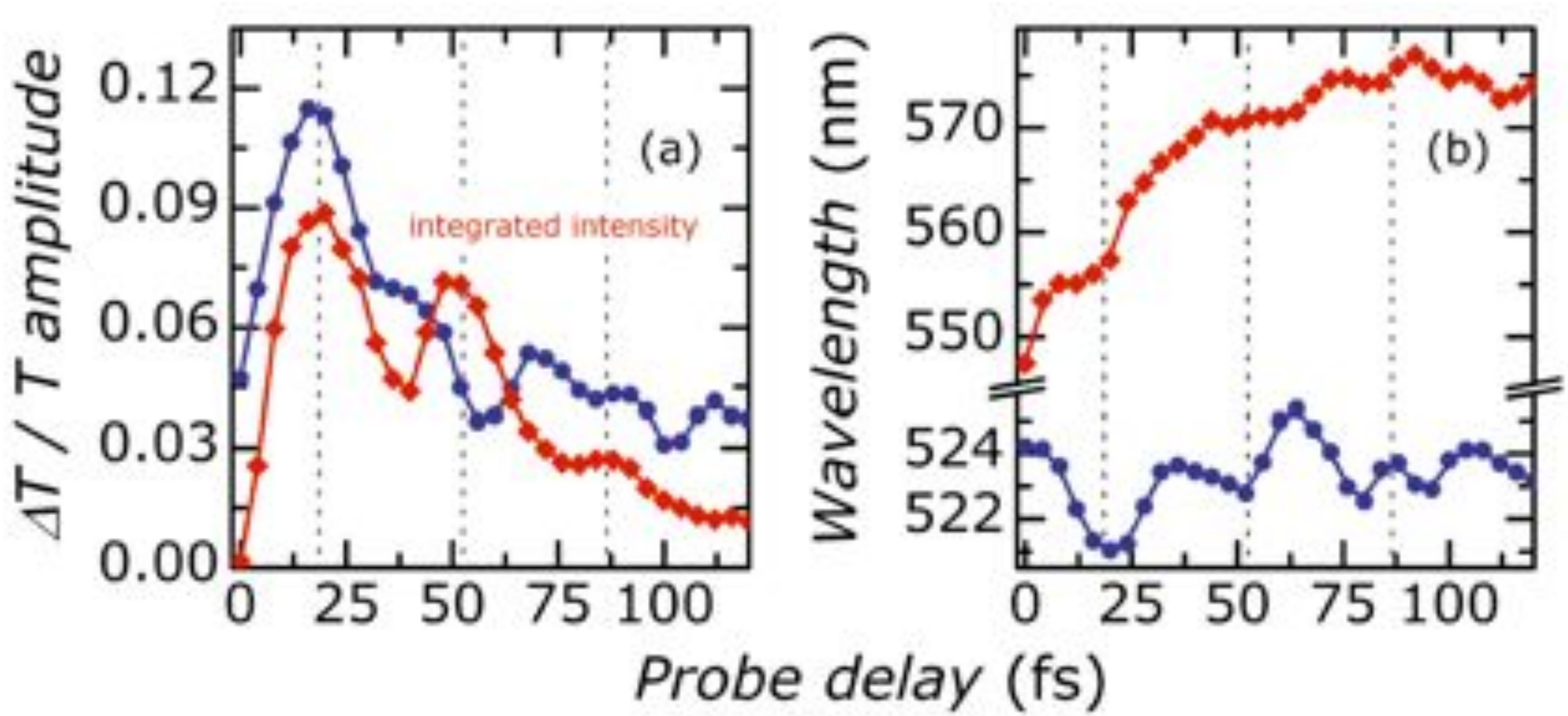
Transient absorption dynamics of the triad



C. A. Rozzi et al., Nature Commun. 4, 1602 (2013).

Transient absorption dynamics of the triad

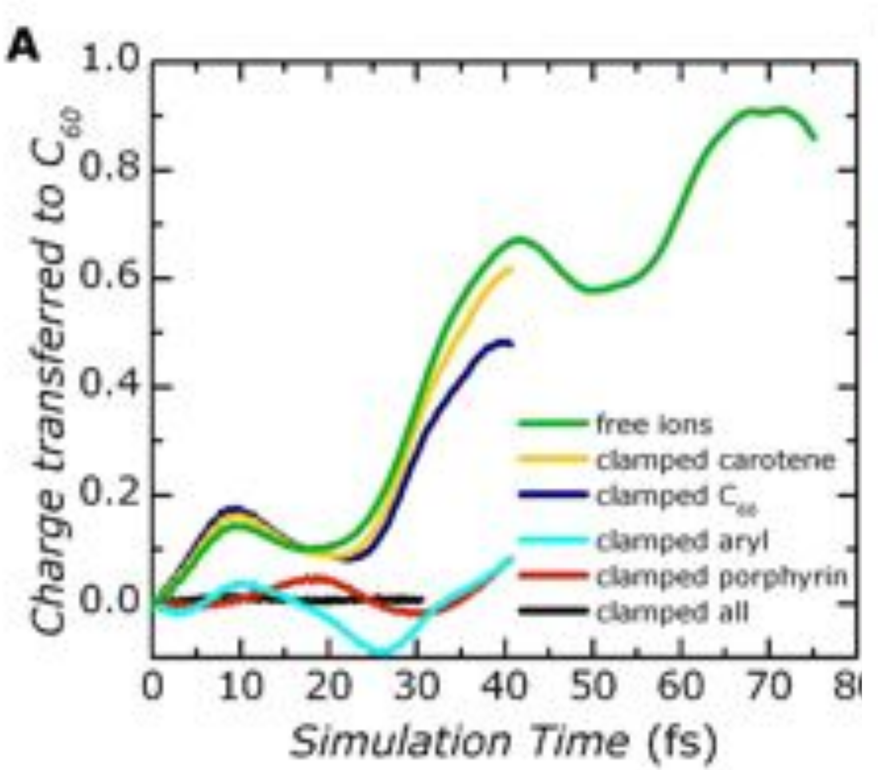
Coherent oscillations of the **resonance wavelength** of the charge transfer band



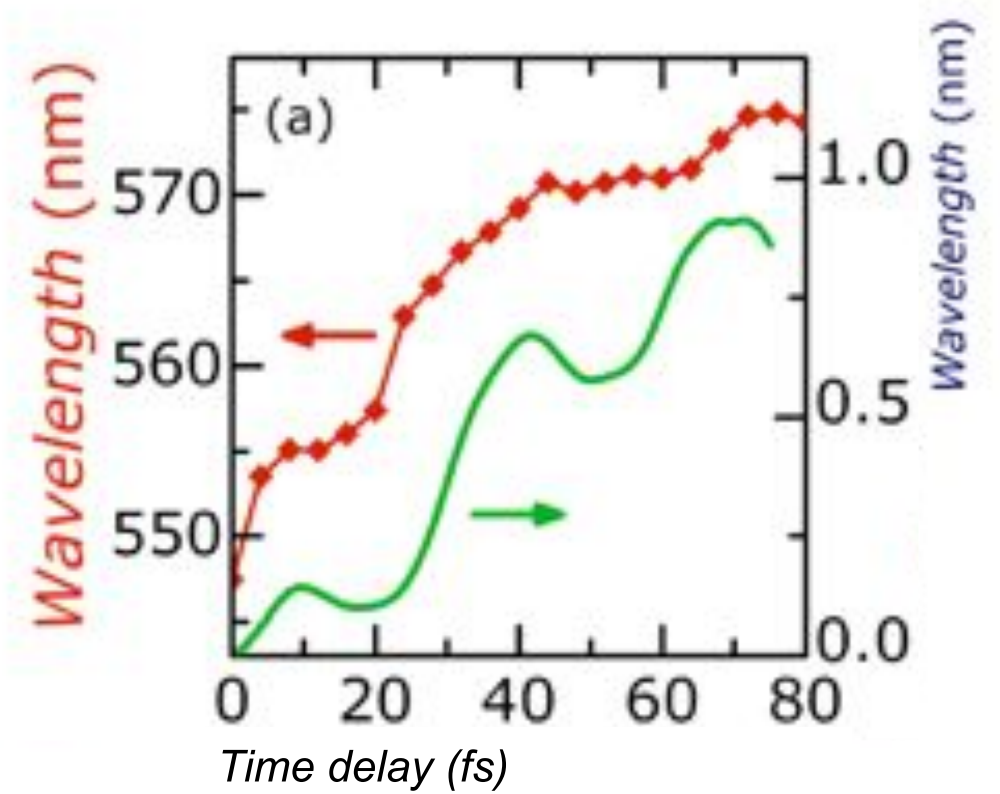
C. A. Rozzi et al., Nature Commun. 4, 1602 (2013).

Coherent charge oscillations: theory and experiments

DFT Calculations

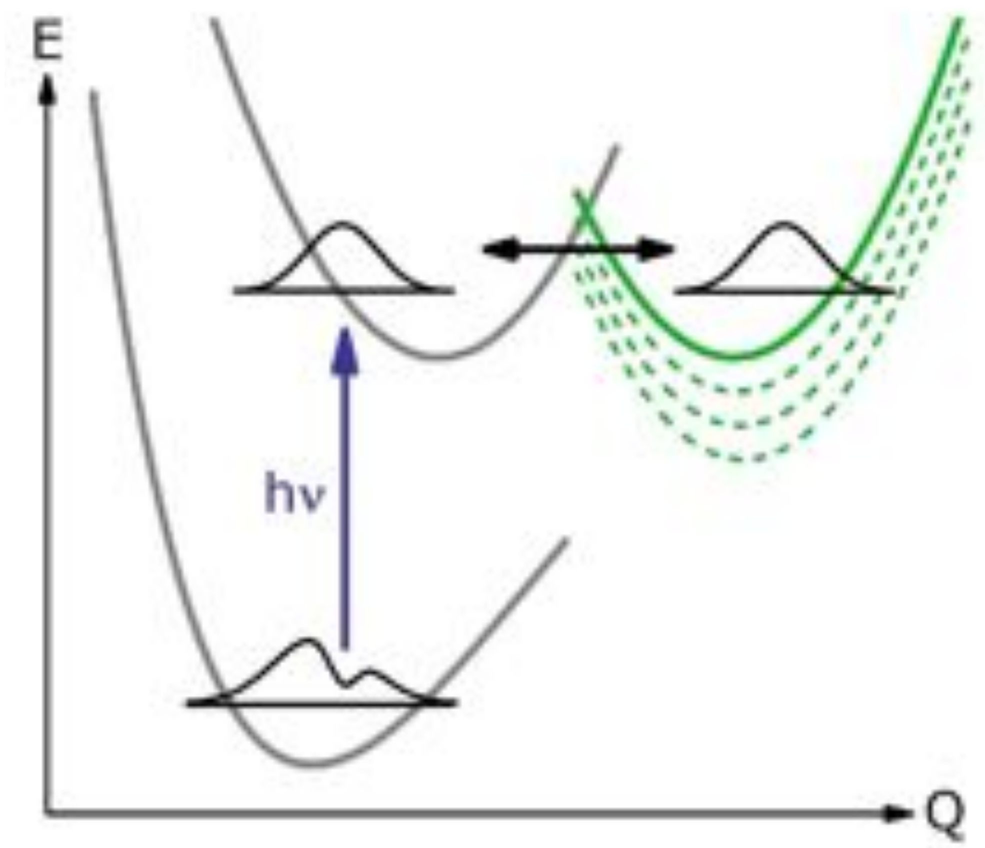


Comparison Experiment-DFT



C. A. Rozzi et al., Nature Commun. 4, 1602 (2013).

Qualitative picture for the electron transfer in the triad



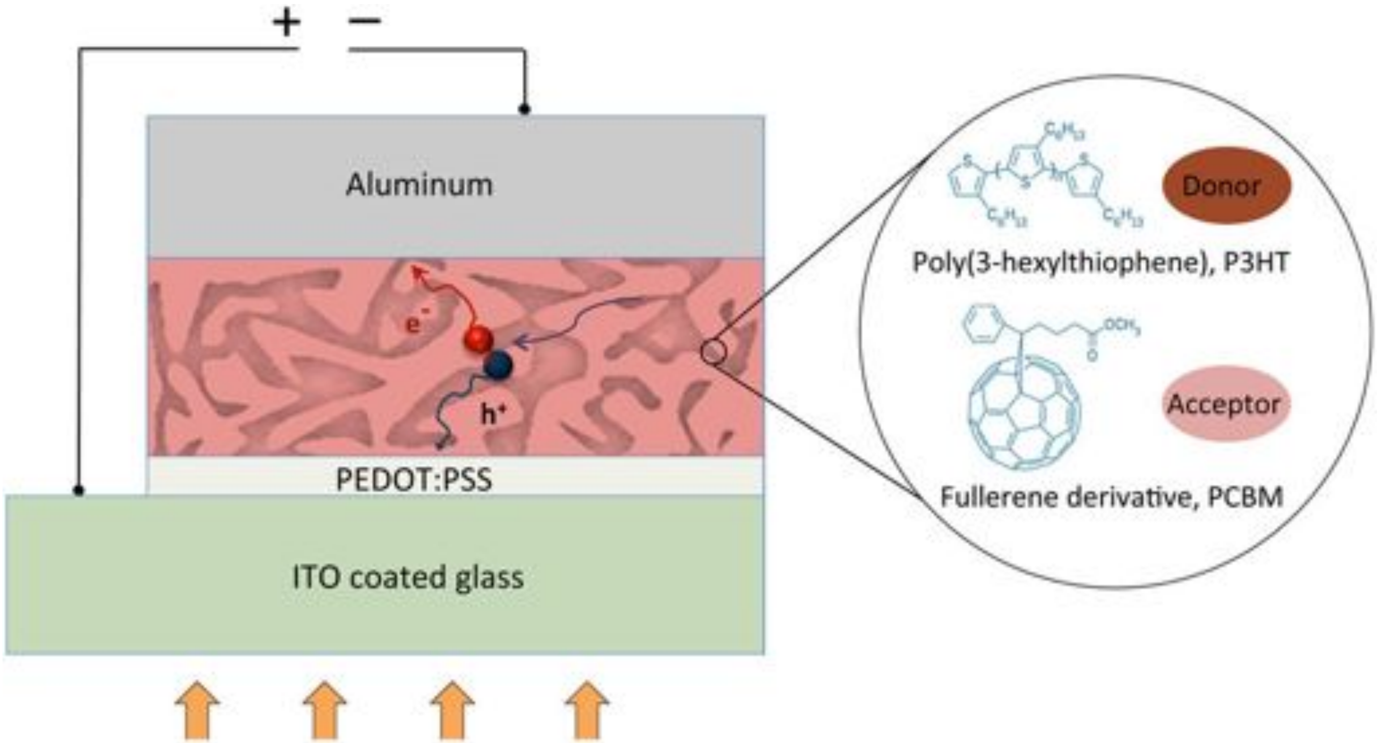
The coupling between electronic and nuclear degrees of freedom is important

Outlook

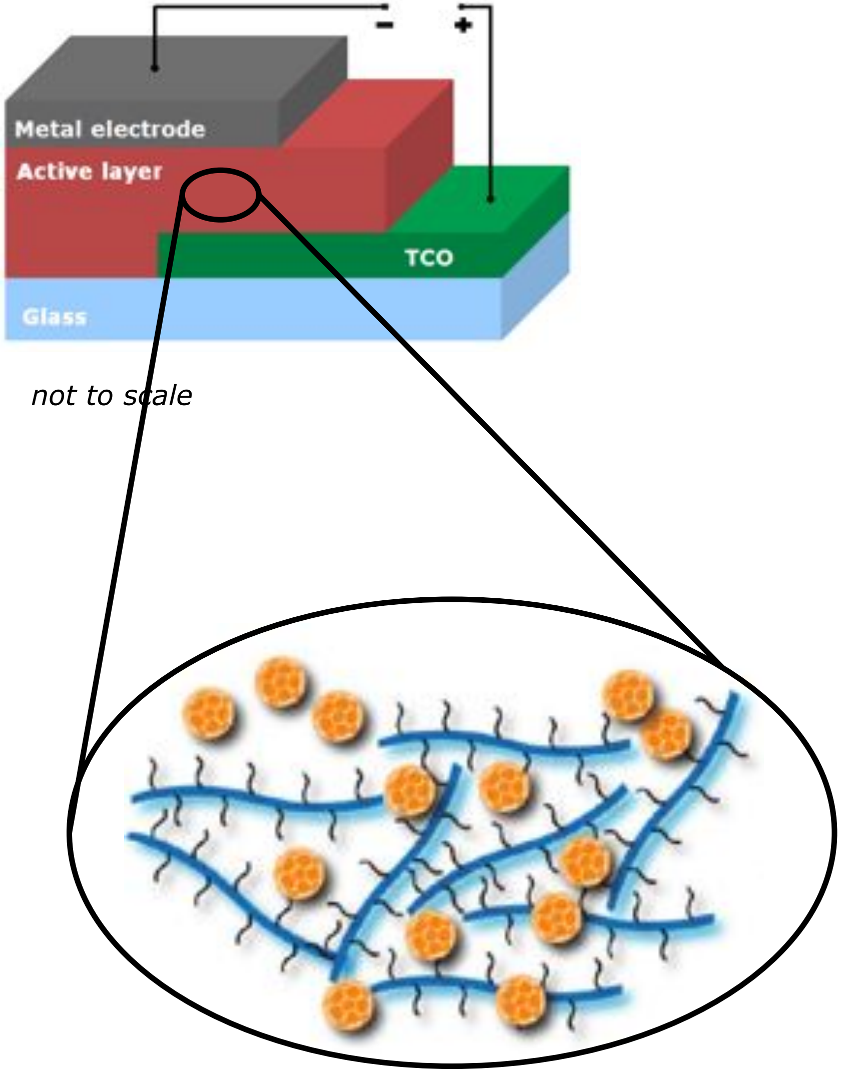
1. Photosynthetic Light Harvesting
2. Ultrafast spectroscopy
3. Natural Light-Harvesting complexes: purple bacteria
4. Artificial Light-Harvesting complexes: dyads and triads
5. Organic photovoltaic (OPV) devices: bulk heterojunctions

Basic working principle of an organic solar cell

- **Absorption** of a photon leads to the formation of an exciton in the polymer
- **Exciton Diffusion** to a polymer:acceptor interface (if necessary)
- **Exciton Dissociation** leading to spatially separated charges
- **Charge Transport** to the electrodes

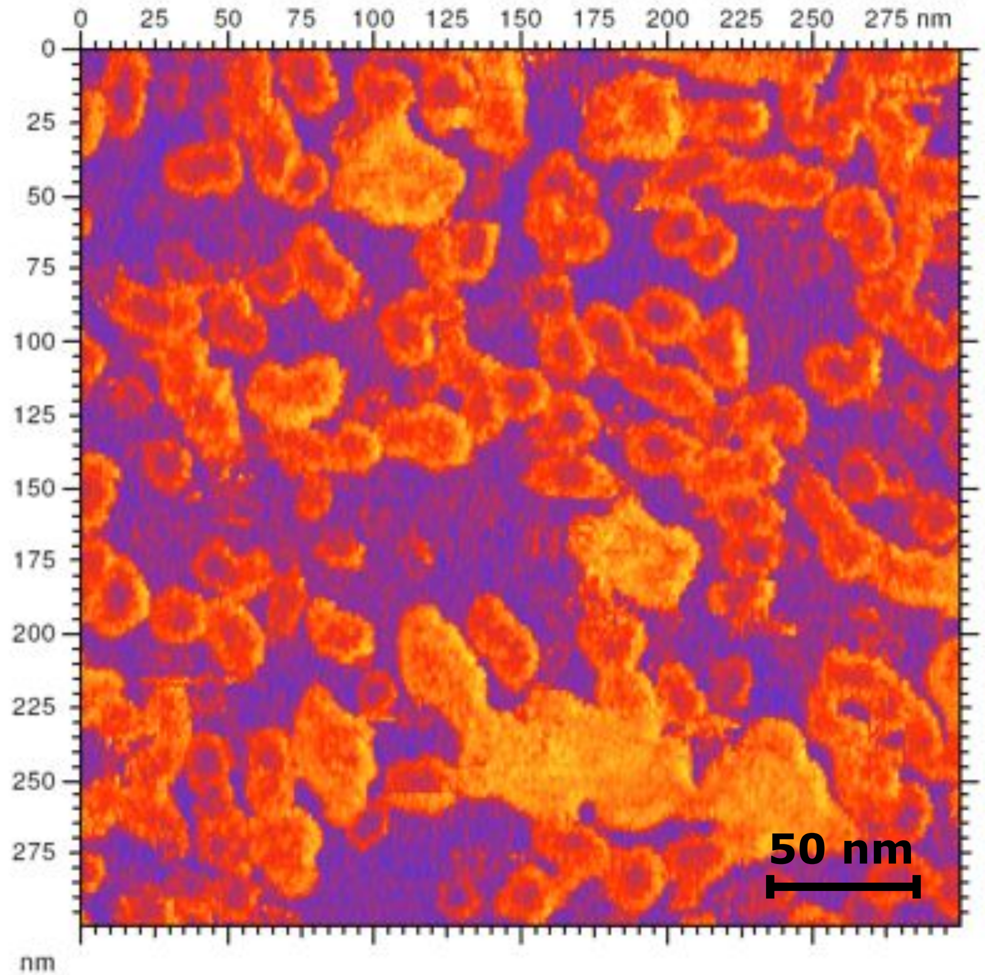


Bulk heterojunction solar cells

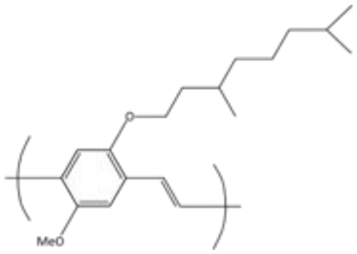


not to scale

AFM phase image

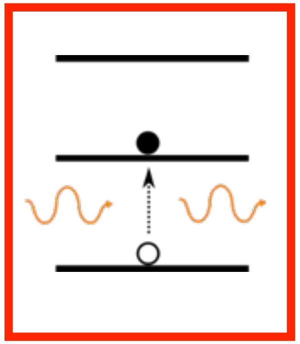


A prototype system: PPV/PCBM

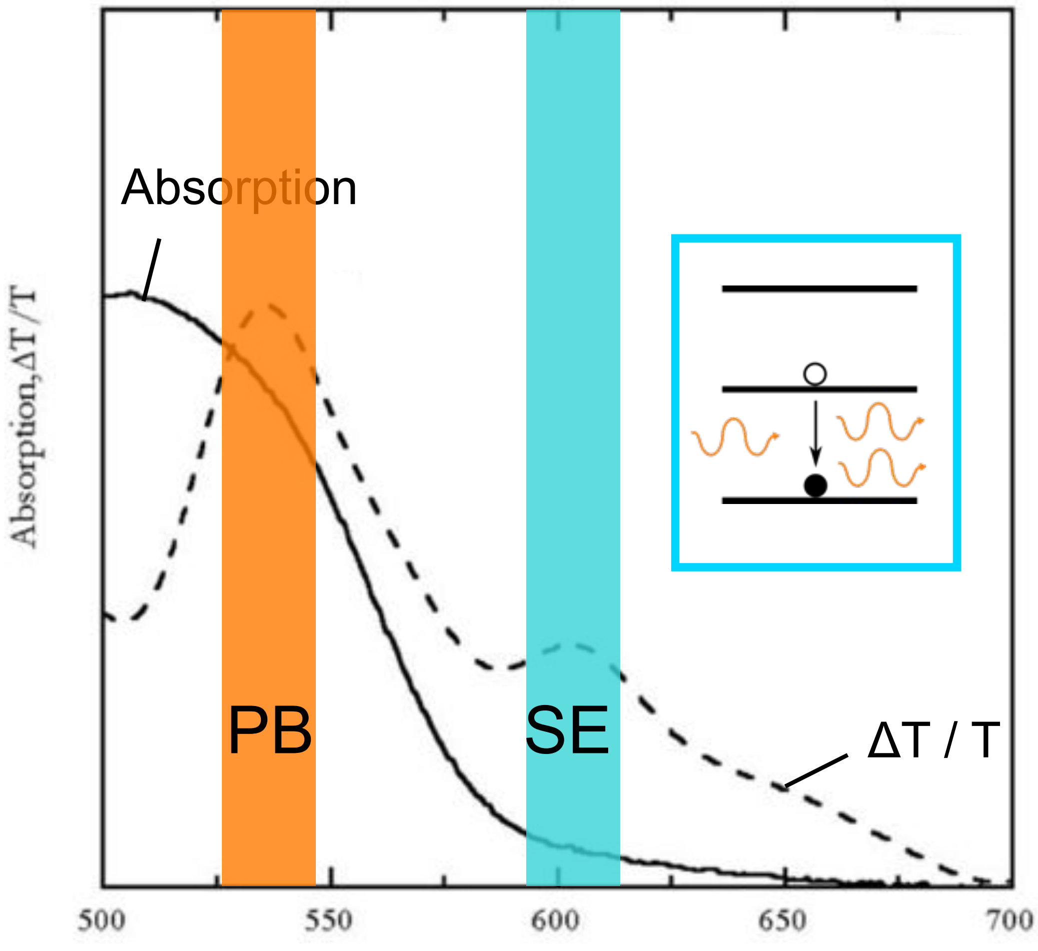


solid line: absorption spectrum of MDMO-PPV

dashed line: differential transmission spectrum ΔT / T of MDMO-PPV at 200 fs delay

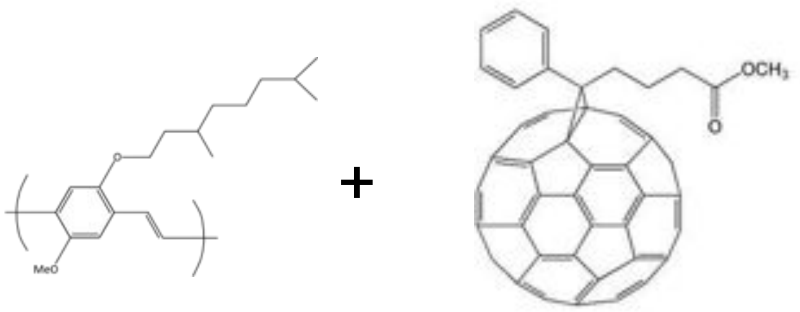


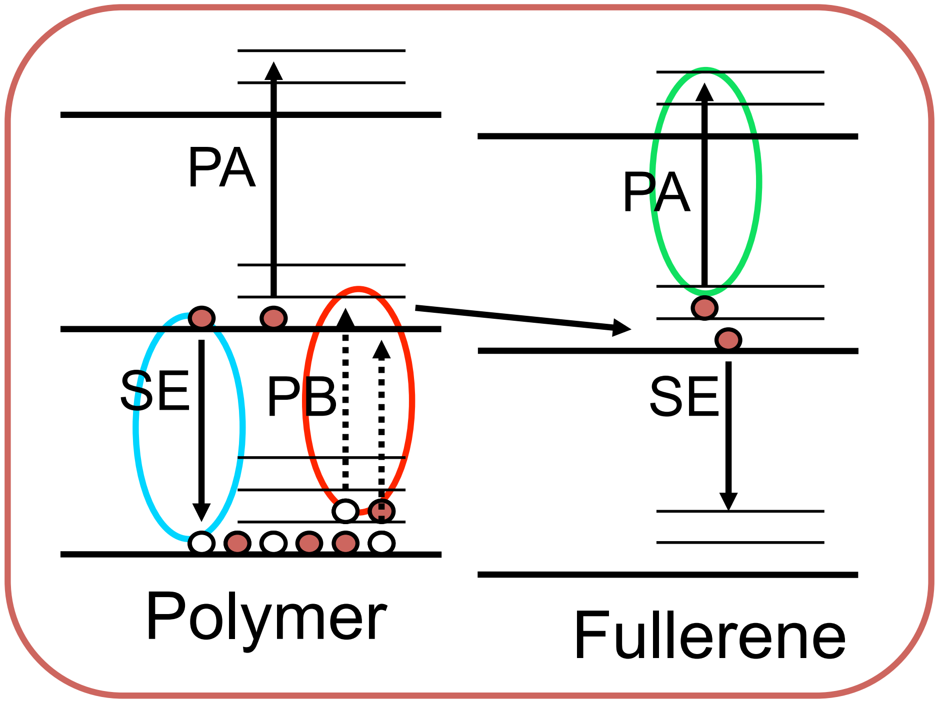
Pure Polymer MDMO-PPV

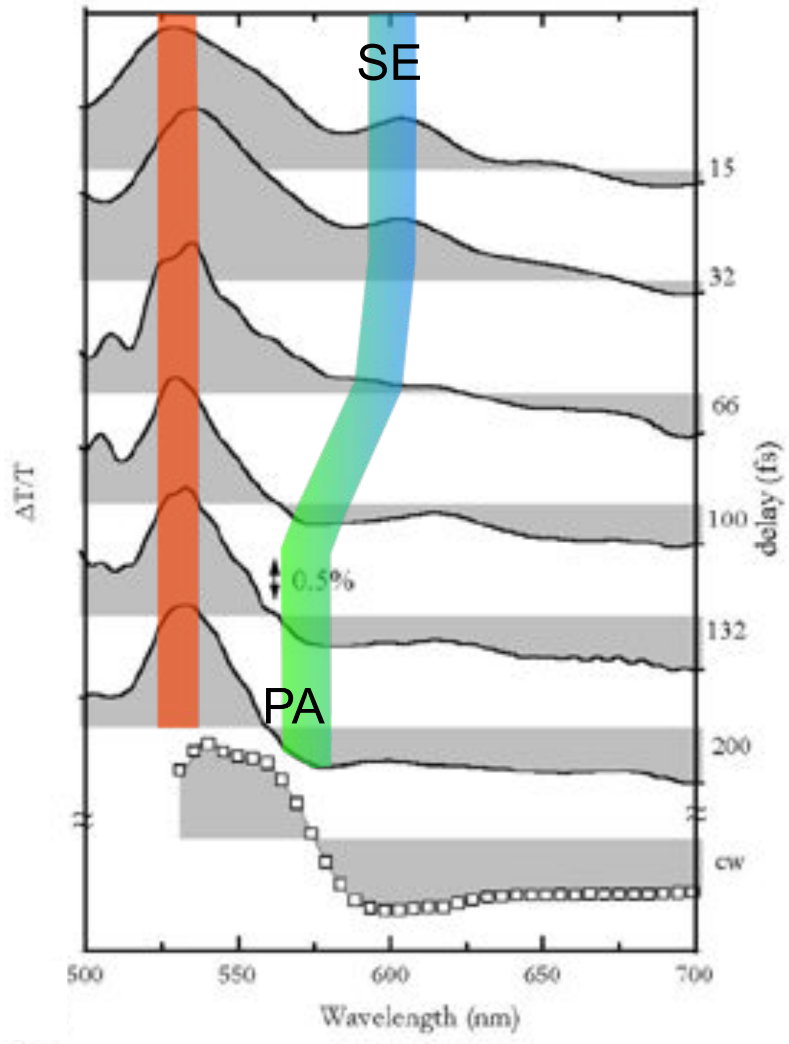


C. J. Brabec, G. Cerullo et al., *Chemical Physics Letters*, 340, 232 (2001).

A prototype system: PPV/PCBM

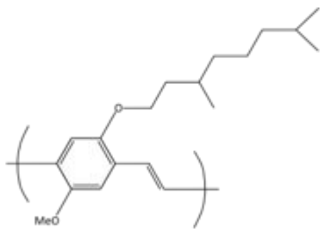






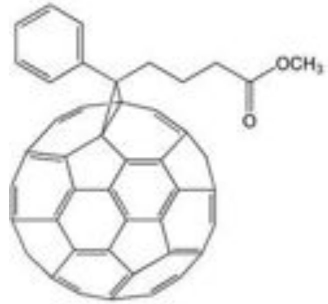
C. J. Brabec, G. Cerullo et al., *Chemical Physics Letters*, 340, 232 (2001).

Photoinduced electron transfer in PPV/ PCBM

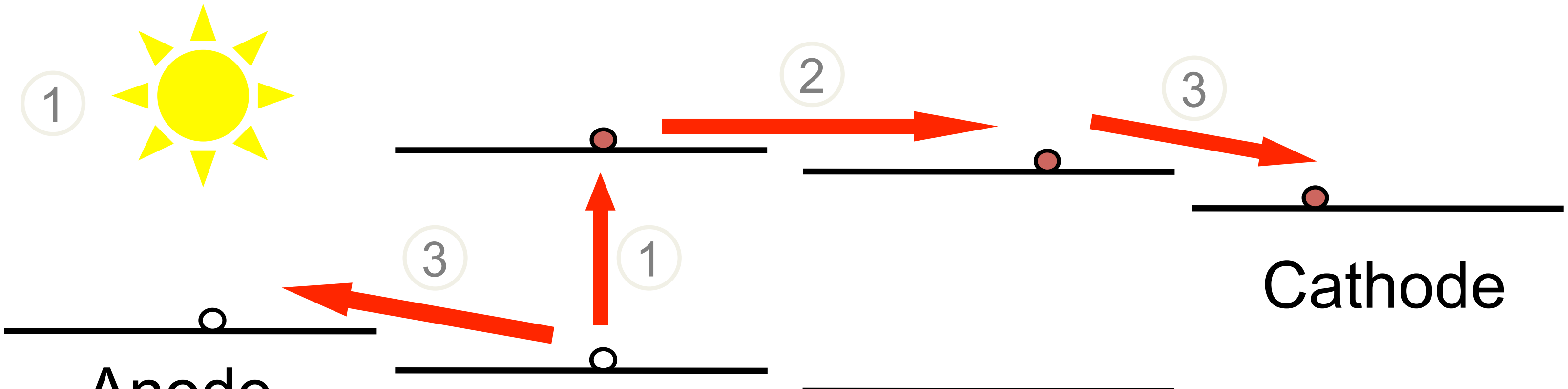


MDMO-PPV

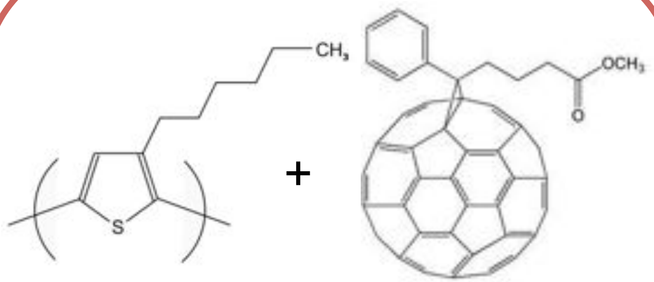
Electron transfer with~ 50 fs time constant



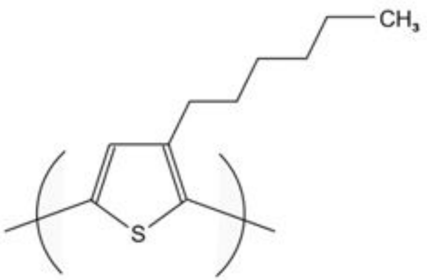
PCBM



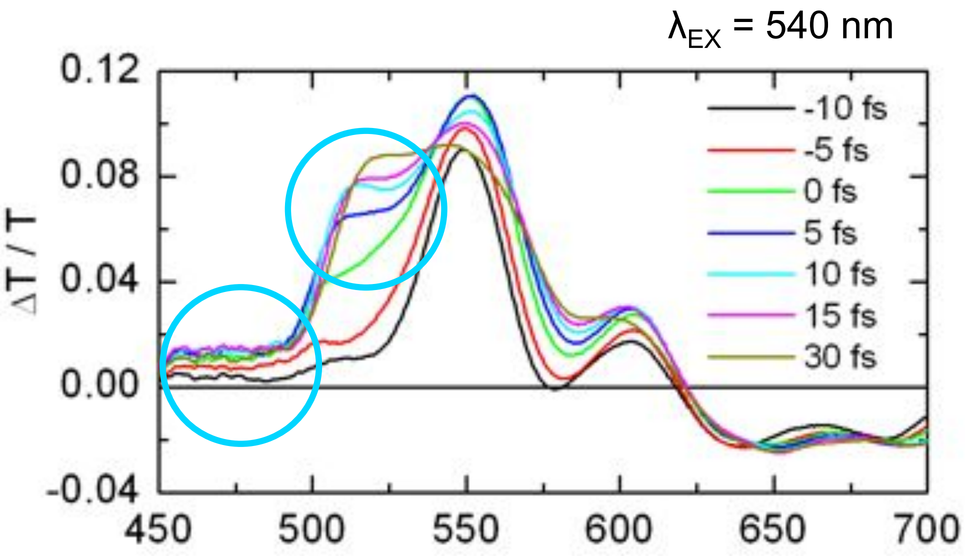
Photoinduced electron transfer in P3HT/PCBM



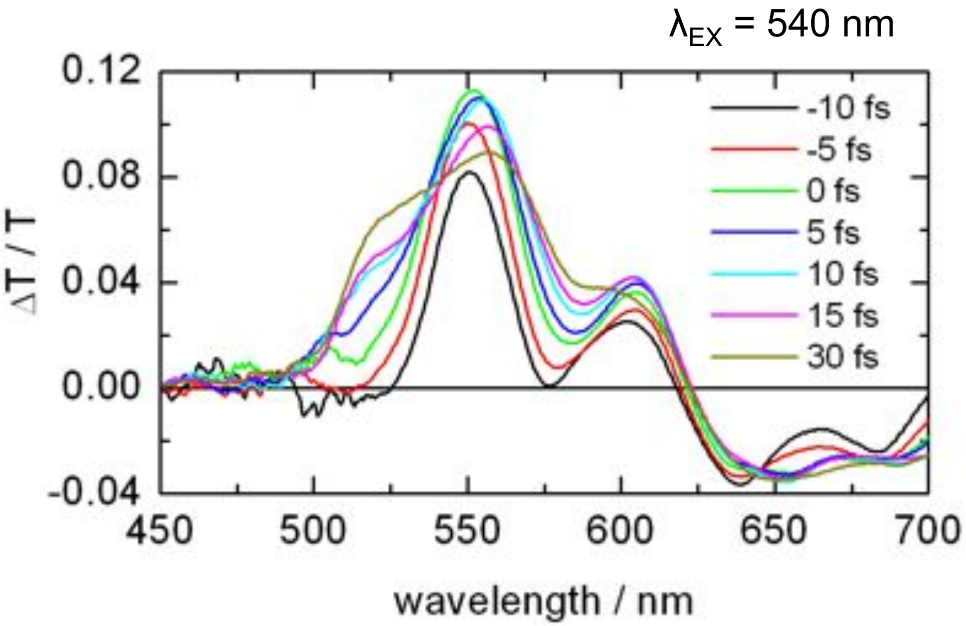
P3HT PCBM



P3HT
poly(3-hexylthiophene)



Blend



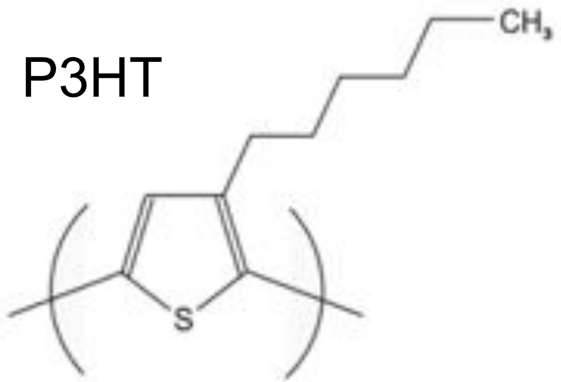
pure Polymer

Pump-probe spectroscopy of P3HT/PCBM

520 nm - 498 nm

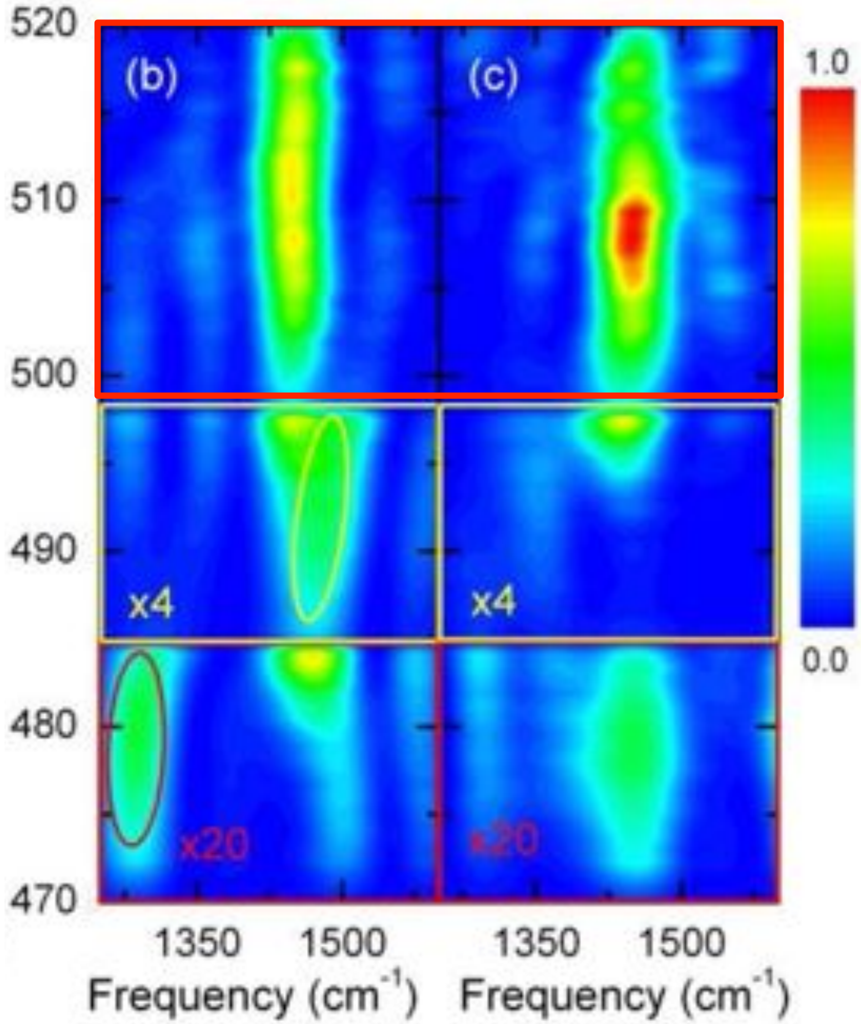
Polymer

P3HT



Vibration at **1450 cm^{-1}** corresponds to the symmetric C=C stretch mode in the polymer

P3HT:PCBM P3HT

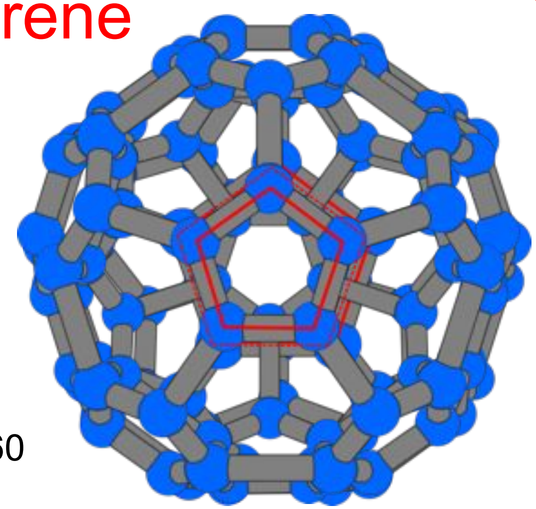


Resonant excitation of the polymer moiety

Pump-probe spectroscopy of P3HT:PCBM

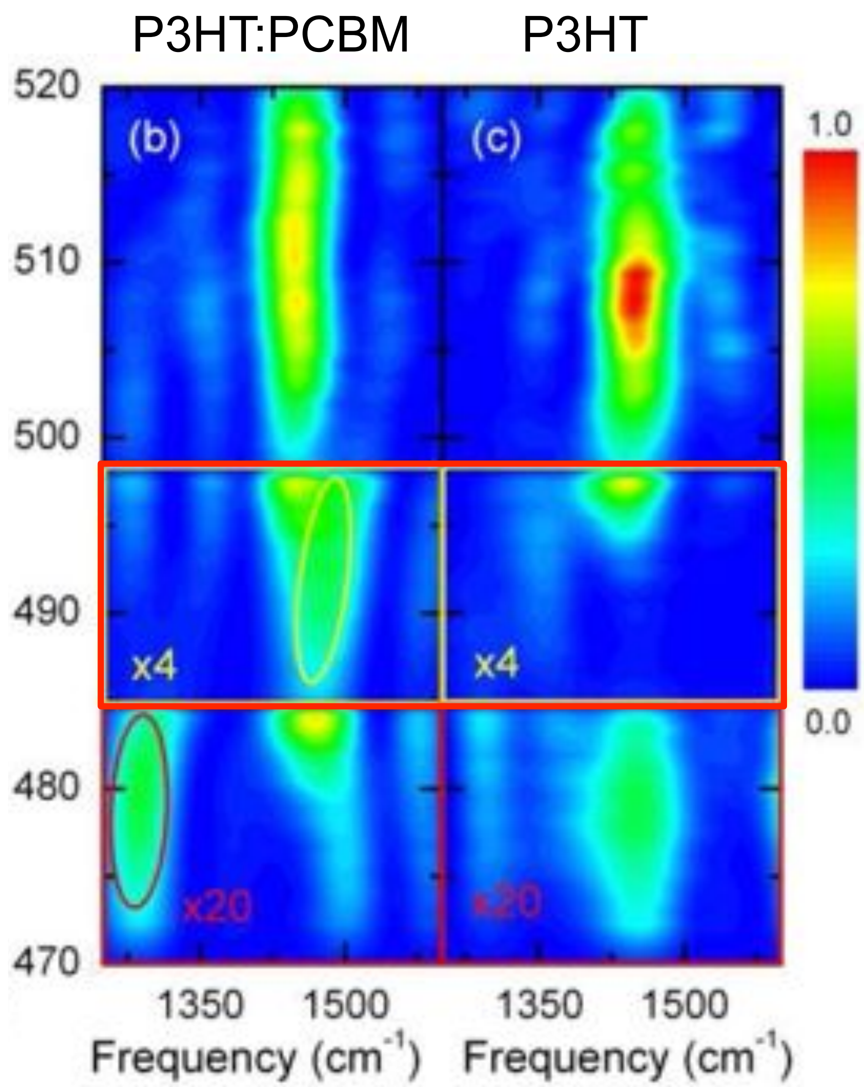
498 nm - 485 nm

Fullerene



C_{60}

Vibration at **1470 cm^{-1}** corresponds to the pentagonal pinch mode of the fullerene

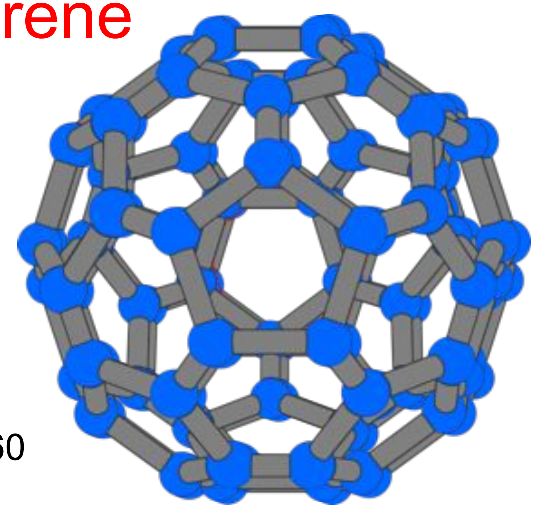


S. M. Falke et al., Science, in press (2014)

Pump-probe spectroscopy of P3HT/PCBM

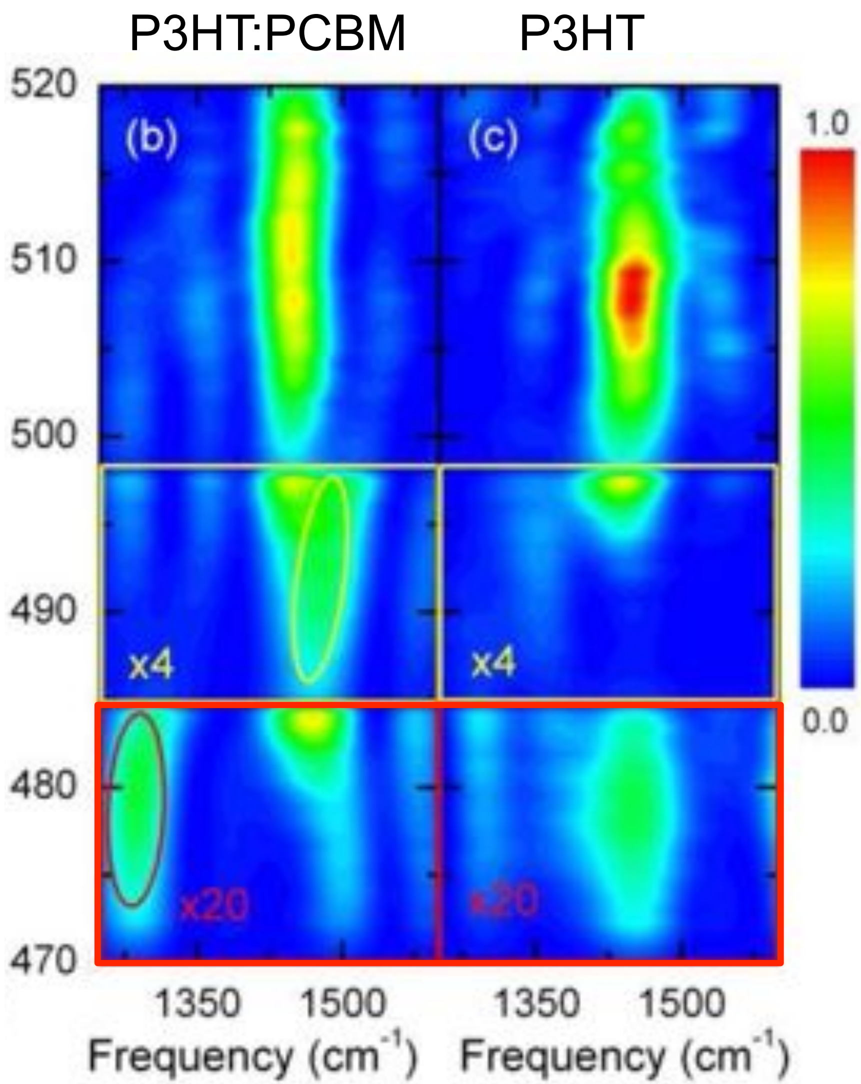
485 nm - 470 nm

Fullerene



C_{60}

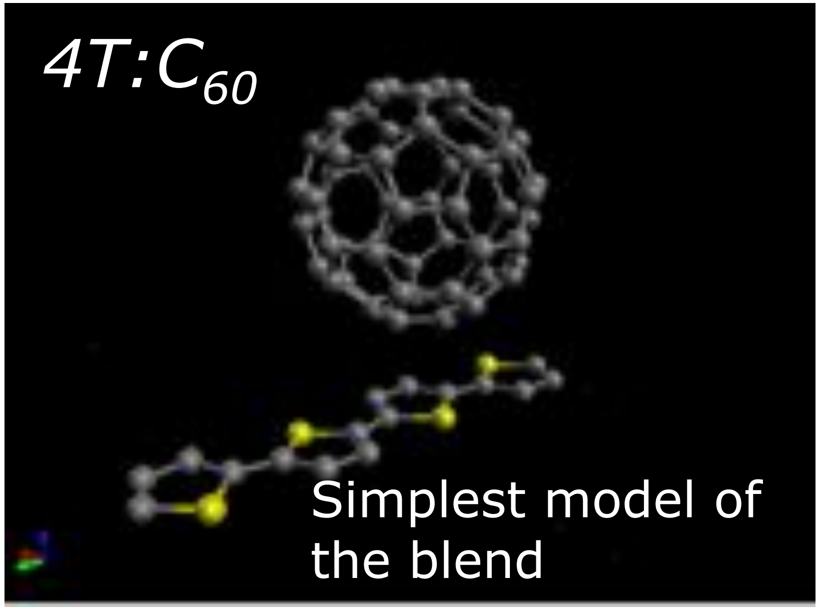
Vibration at **1289 cm^{-1}** corresponds to the $T_{1g}(3)$ mode of the fullerene molecule



Theoretical modelling

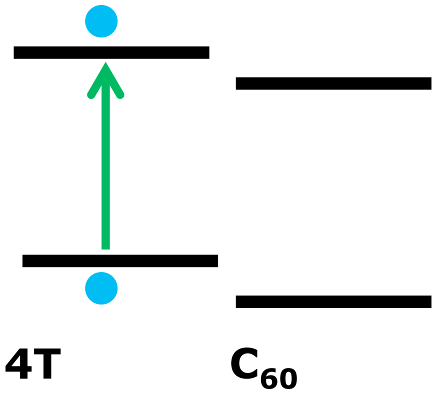
Density functional theory (DFT) calculations suggest that the electron transfer in P3HT:PCBM proceeds via an extended electronic bridging state (Kanai and Grossmann 2007).

Y. Kanai, J.C. Grossman, *Nano Letters* **7**, 1967, (2007)



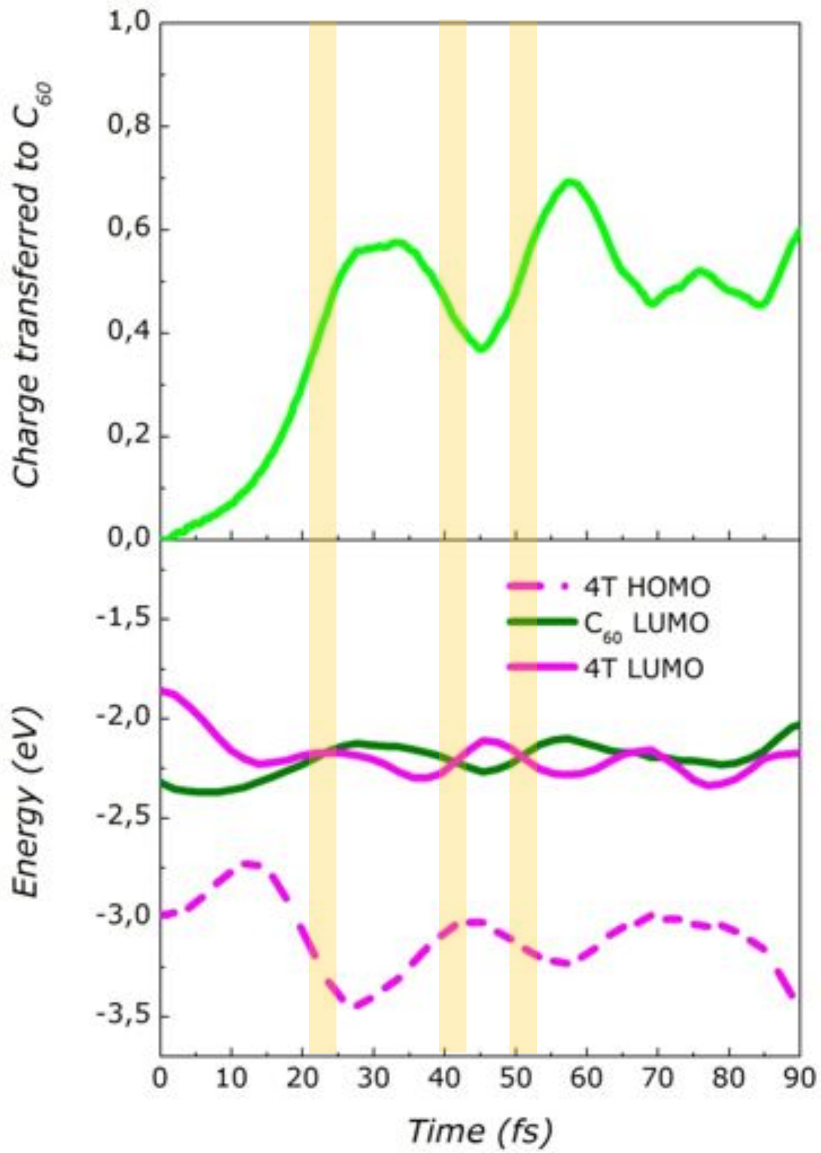
Here:
we use ab initio ***time-dependent DFT*** *to describe the dynamics of electrons and nuclei following light absorption.*

Time dynamics of the charge transfer



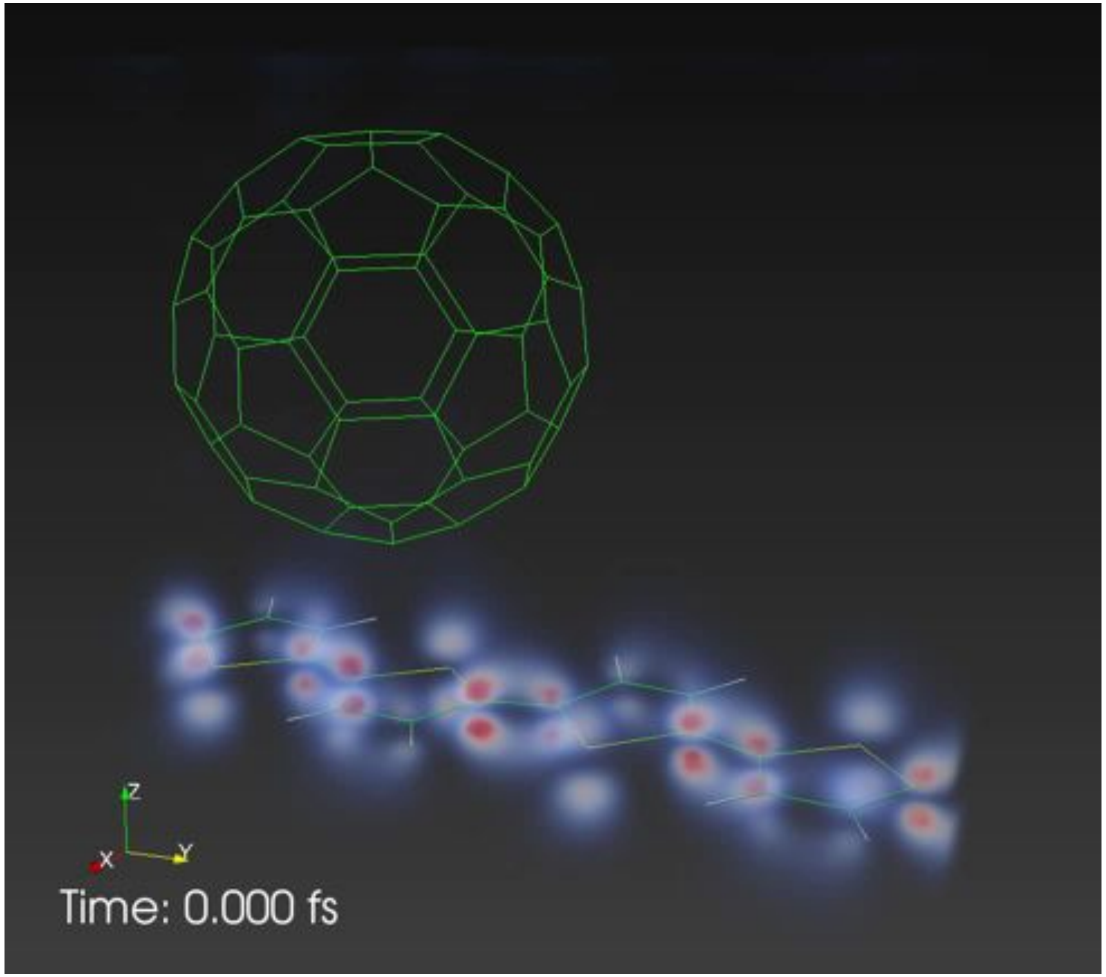
t = 0 fs

- Charge transfer probability oscillates with a period similar to that of vibrational motion
- The coupling between electrons and phonons is most essential for driving the charge transfer



S. M. Falke et al., Science, in press (2014)

Time dynamics of the charge transfer



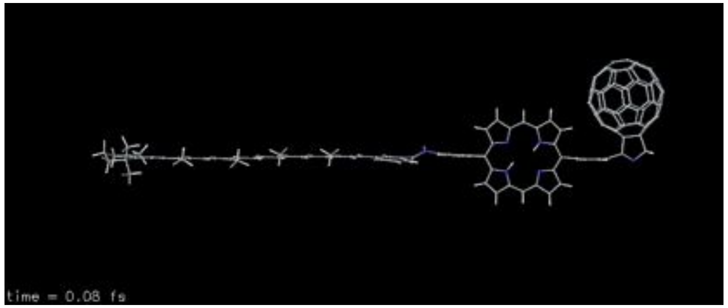
Time evolution of the electronic density and the nuclear configuration

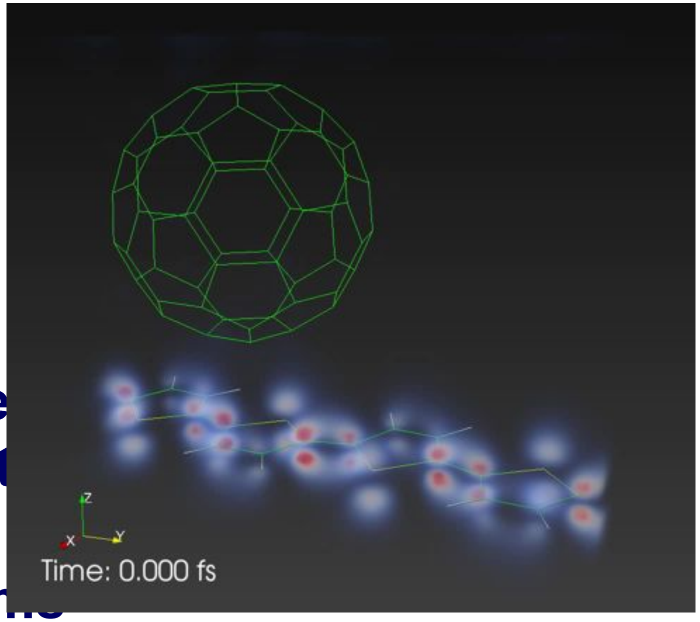
Summary

- **Two different case studies for quantum-coherent charge transfer dynamics**

  Supramolecular C-P-C60 triad (covalently bound)

  Organic solar cell P3HT/PCBM (non-covalently bound)





- **The quantum coherent coupling between electrons and nuclei is of central importance for the charge transfer in artificial light harvesting and organic solar cell systems**

C. A. Rozzi et al., Nat. Comm. 4, 1602 (2013)
S. M. Falke et al., Science, in press (2014)

Thanks to…

POLITECNICO DI MILANO

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D. Brida
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A. L. Moore

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SINCE 1880 OSAKA CITY UNIVERSITY OCU

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CNRNANO MODENA S3

CARL VON OSSIETZKY universität OLDENBURG

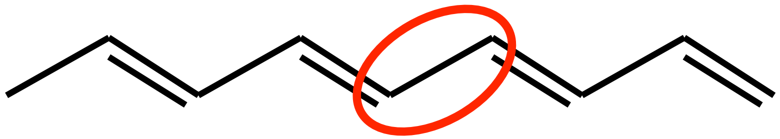
Ch. Lienau

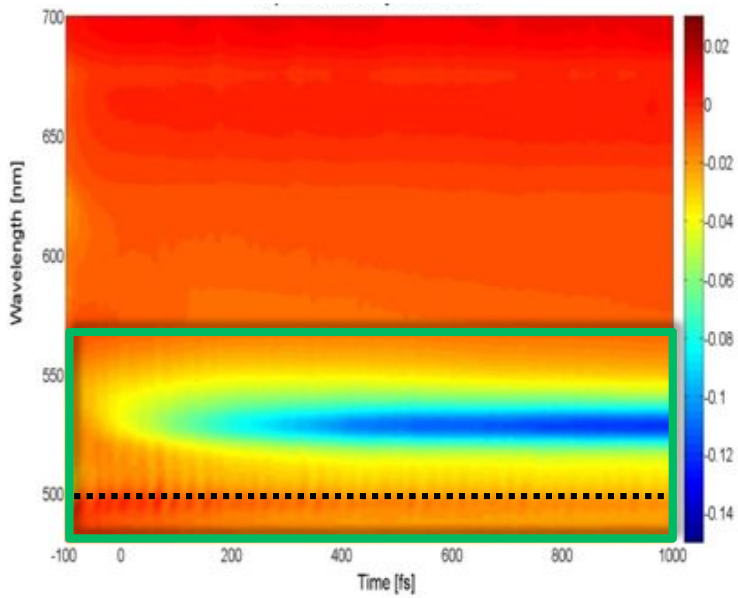

THANK YOU!!!

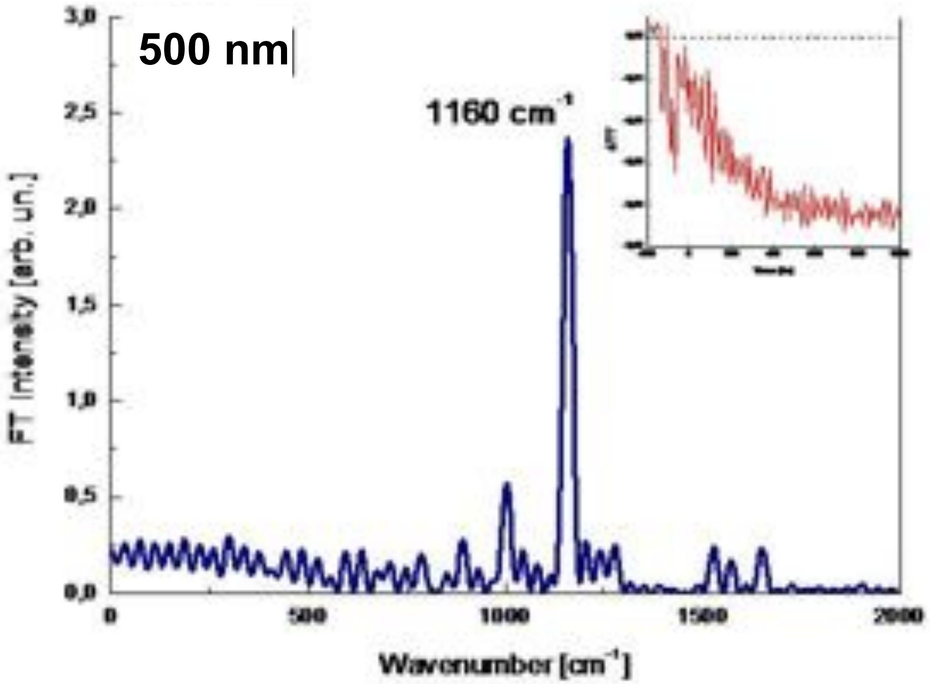
Ground State Oscillations in Cyclohexane

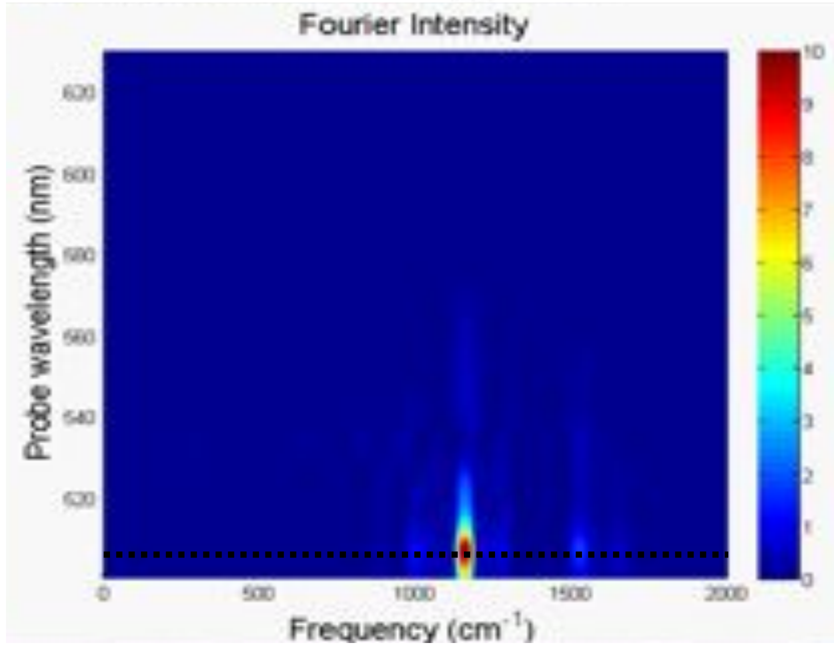
• Observation of coherent nuclear motion of the carbon backbone

≈ 30 fs





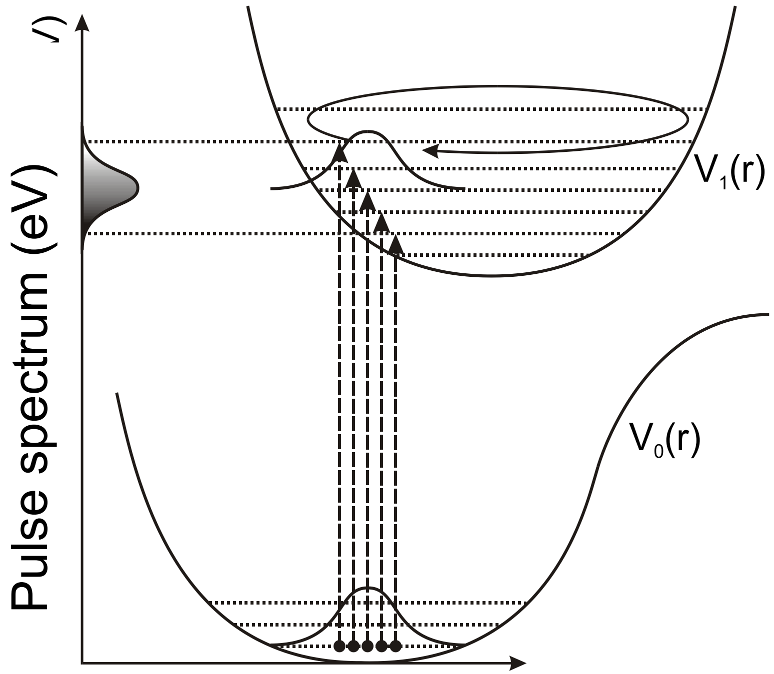




Coherent nuclear motion - 1

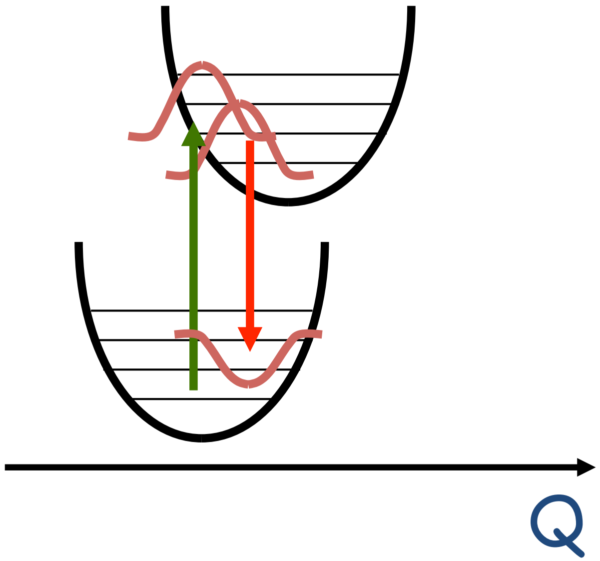
- Observation of **coherent nuclear motion** of the carbon backbone

- Creation of **excited-state** coherence



Coherent nuclear motion - 2

- **Ground state** coherence after second-order pump interaction



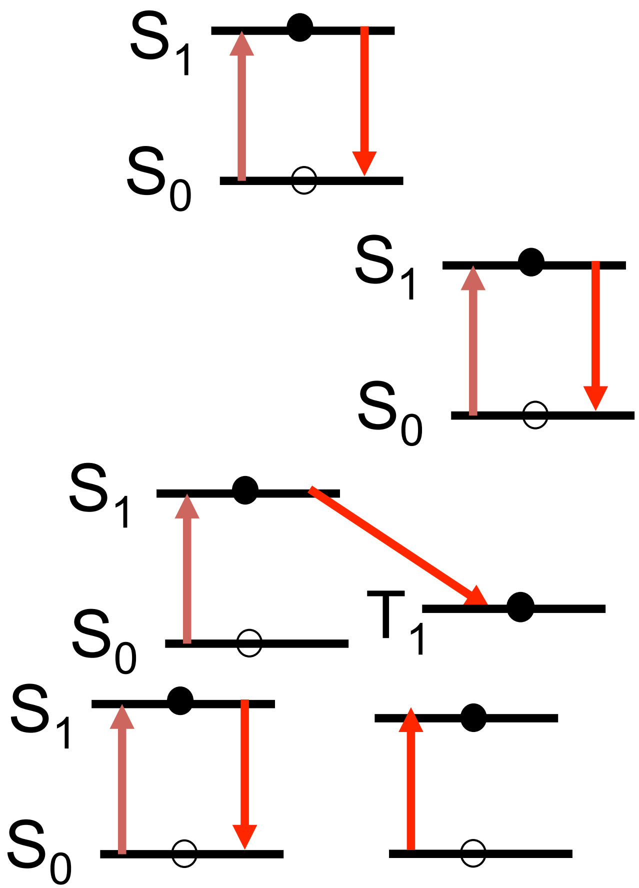
Nuclear motion takes place during excitation

Impulsive Stimulated Raman Scattering

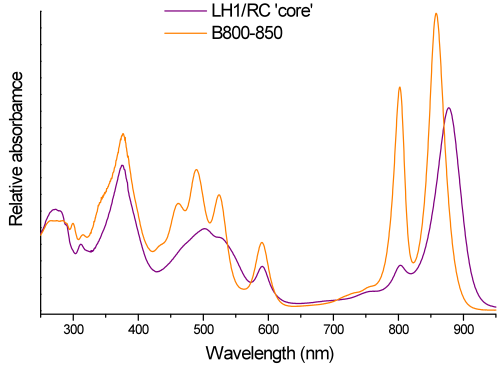
W.T. Pollard *et al*. J.P.C. **96**, 6147 (1992)

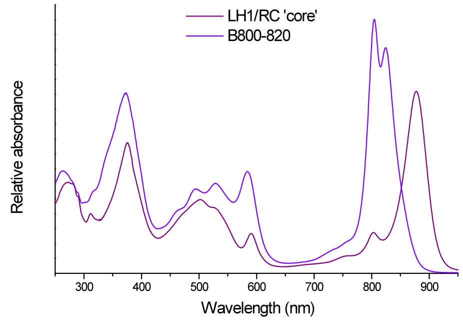
Ultrafast processes in molecular systems

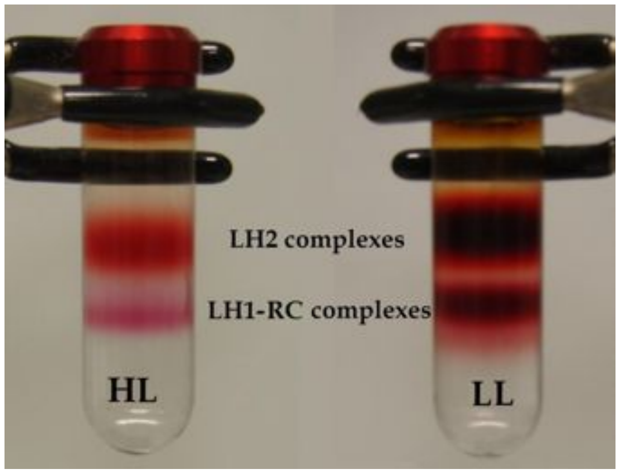
- Excited state radiative decay
- Excited state non-radiative decay (internal conversion)
- Inter-system crossing to the triplet state
- Energy transfer to another molecule
- Charge transfer to another molecule

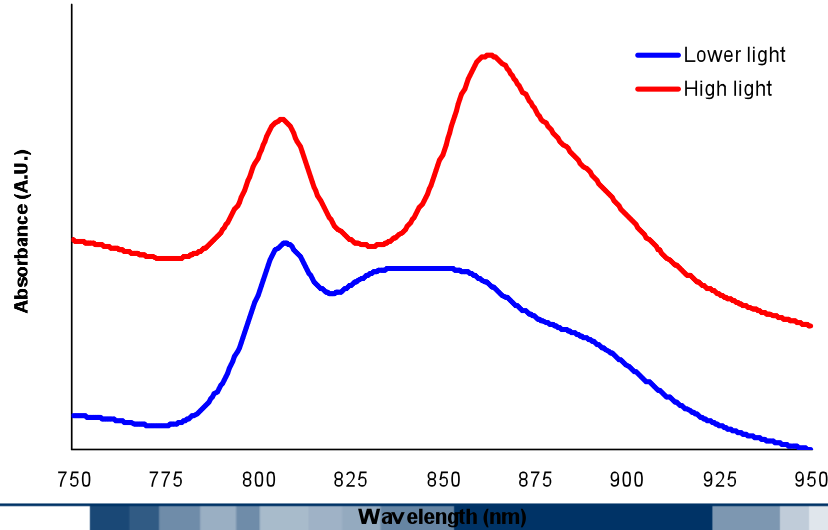


Photosynthetic bacteria grown in different light intensities

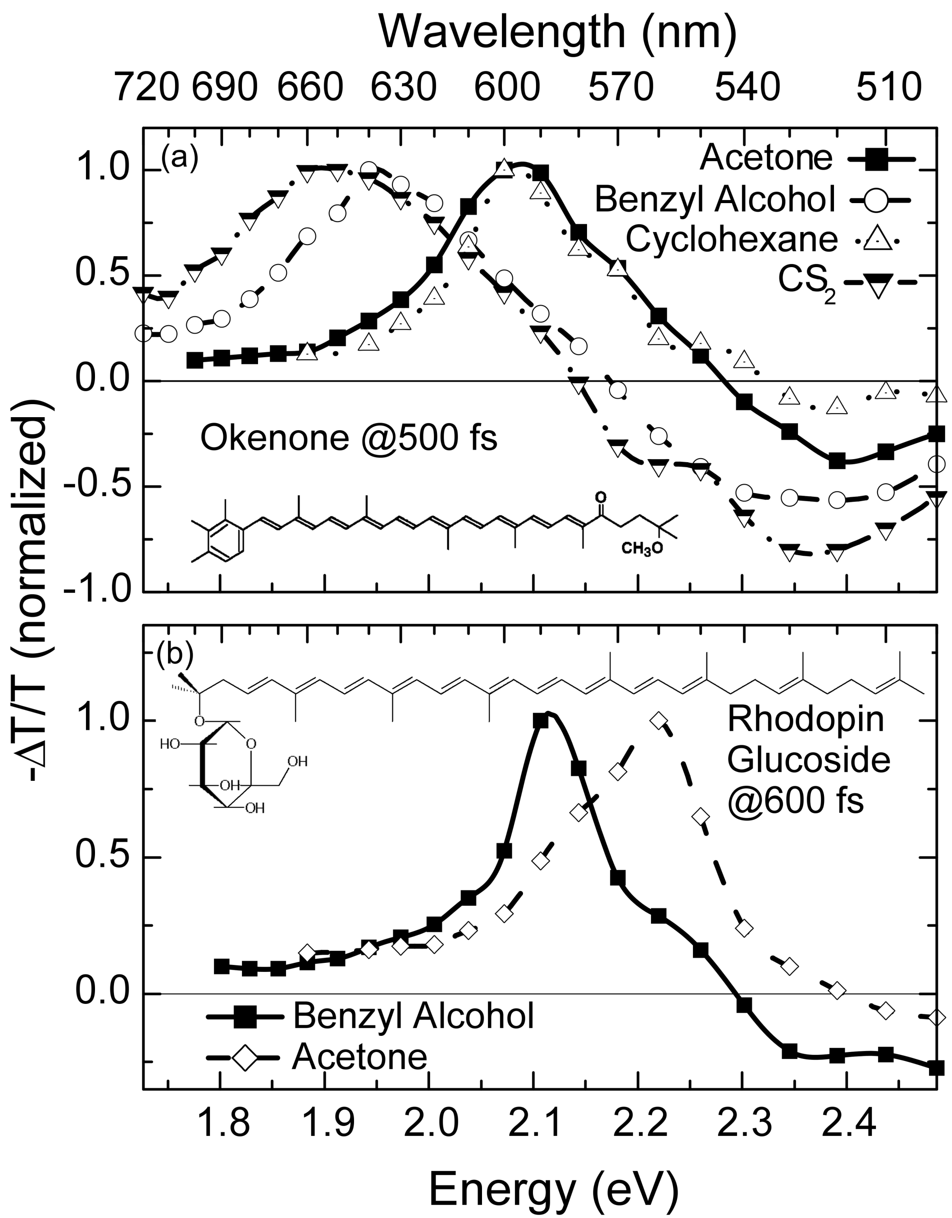






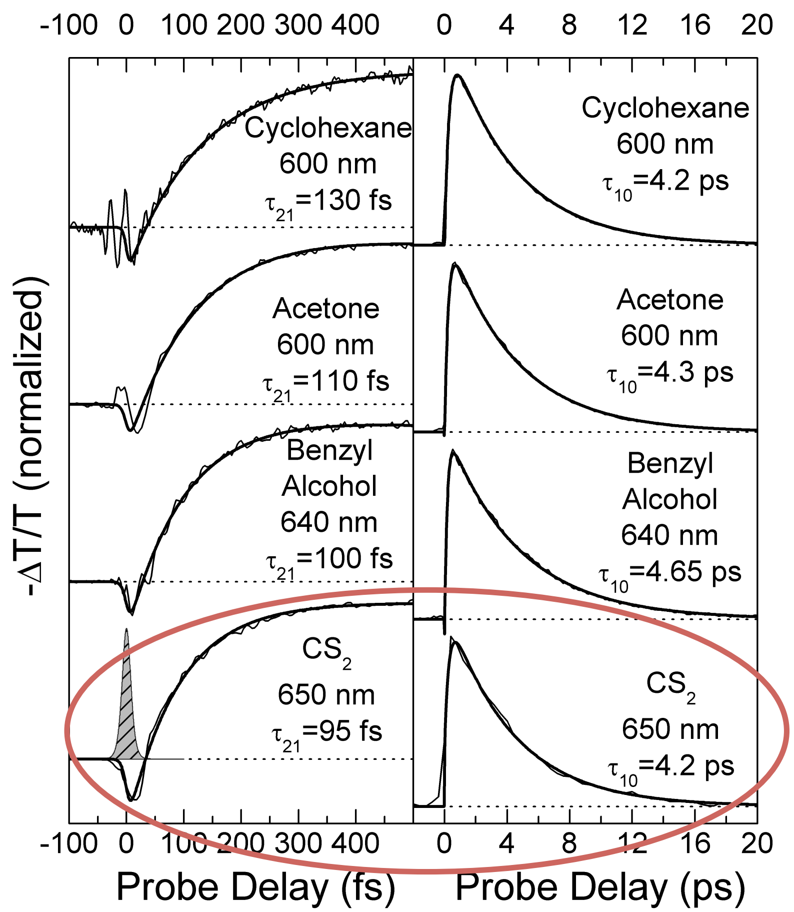


Pump-Probe spectra in various solvents

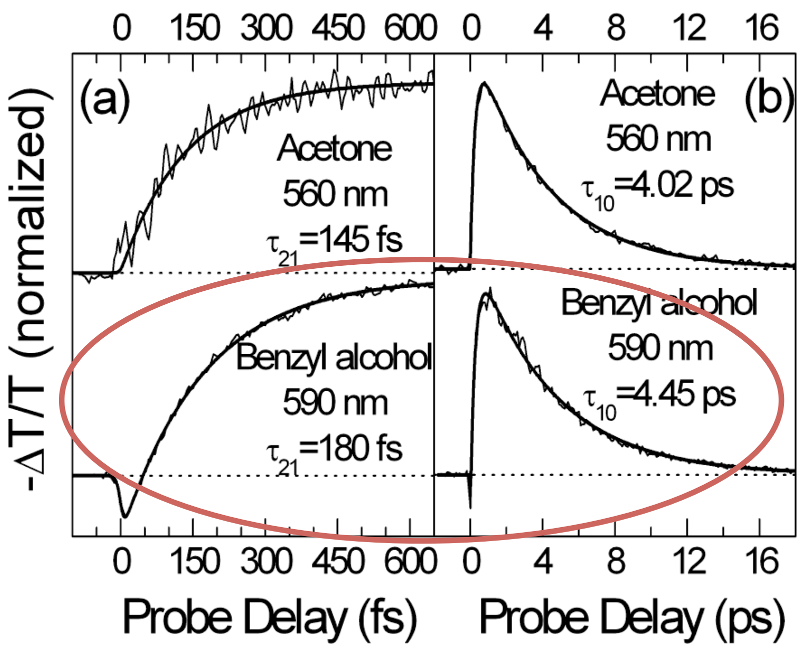


Pump-Probe dynamics in various solvents

Okenone

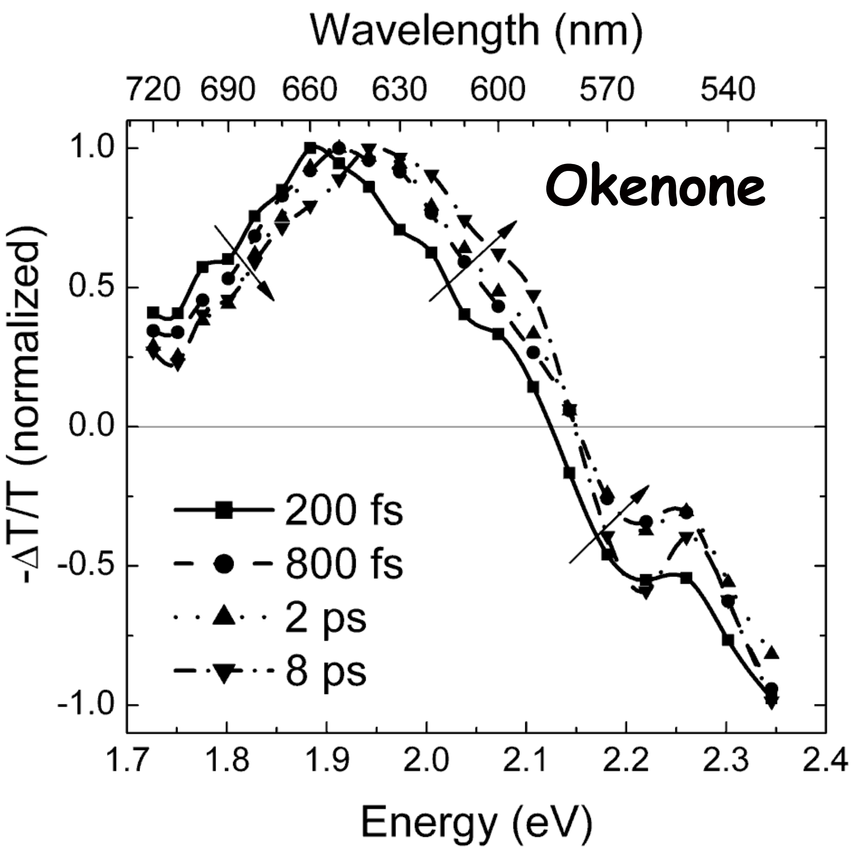


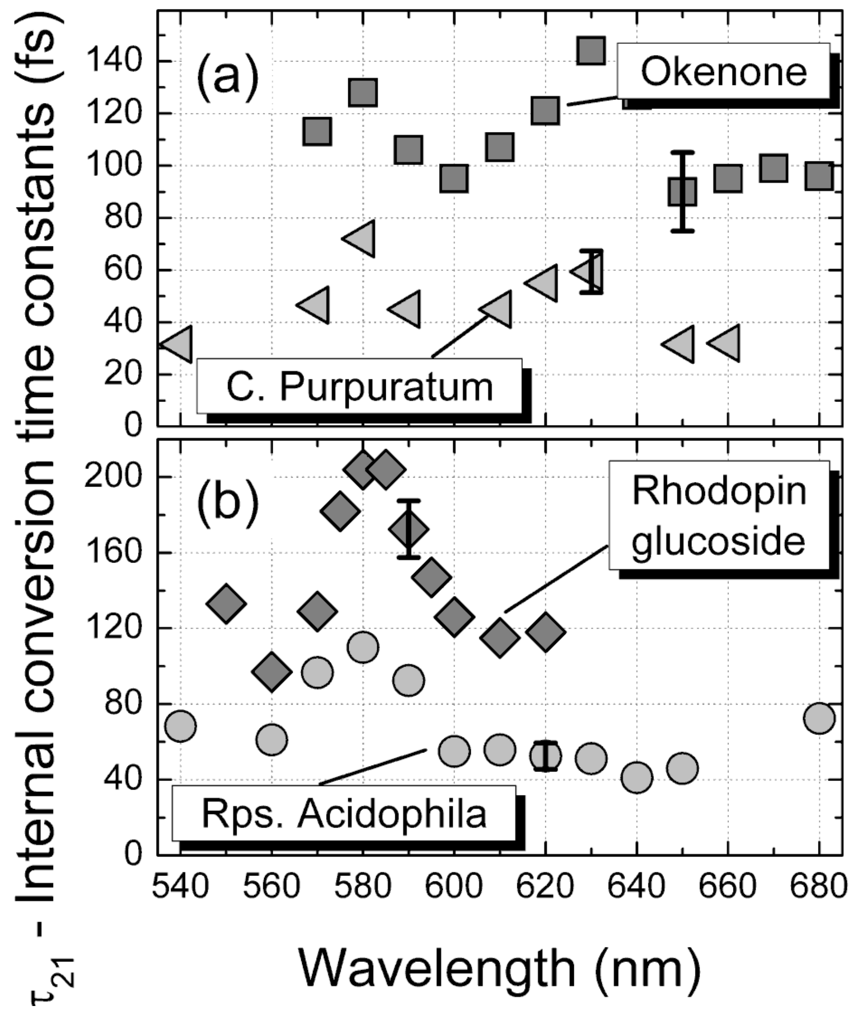
Rhodopin glucoside



Sample	Solvent	PA_1 band peak wavelength	PA_1 formation time constant	PA_1 decay time constant
Okenone	Cyclohexane	600 nm	130 fs	4.2 ps
	Acetone	600 nm	110 fs	4.3 ps
	Benzyl alcohol	640 nm	100 fs	4.65 ps
	CS_2	650 nm	95 fs	4.2 ps
Rhodopin	Acetone	560 nm	145 fs	4.02 ps
glucoside	Benzyl alcohol	590 nm	180 fs	4.45 ps

Problem: wavelength-dependent dynamics





Triad: photoinduced charge transfer dynamics

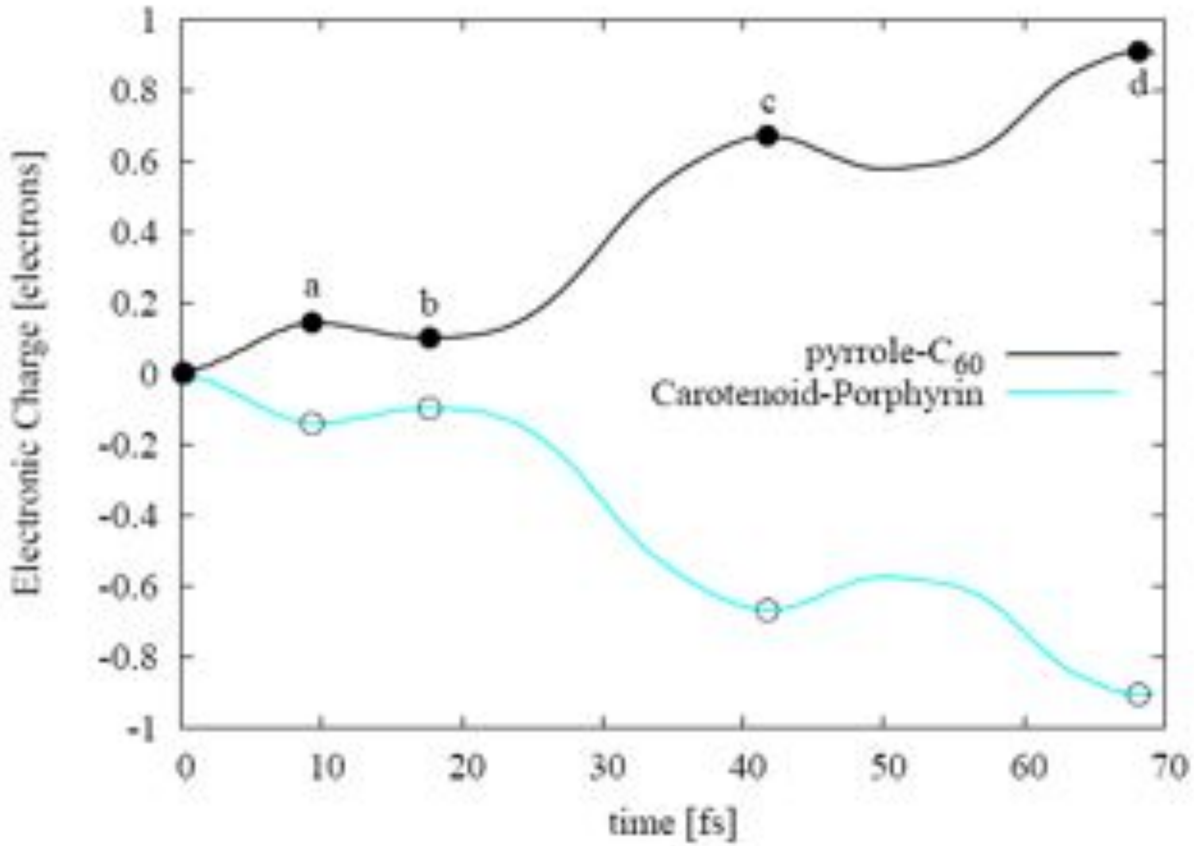


Figure 6.2: Fraction of electrons transfered to the pyrrole-C_{60} part (black line) from the Carotenoid-Porphyrin part (cyan line) of the triad as a function of time after excitation.

Courtesy: Nicola Spallanzani, Franca Manghi and Elisa Molinari (U Modena)

Equations

In solution	Inside LH2

In solution

$$\frac{dN_{20}}{dt} = g(t) - k_{IC21}N_{20};$$

$$\frac{dN_{12}}{dt} = k_{IC21}N_{20} - k_{V2}N_{12};$$

$$\frac{dN_{11}}{dt} = k_{V2}N_{12} - k_{V1}N_{11};$$

$$\frac{dN_{10}}{dt} = k_{V1}N_{11} - k_{IC10}N_{10};$$

$$\frac{dN_{00}}{dt} = -g(t) + k_{IC10}N_{10}.$$

Inside LH2

$$\frac{dN_{20}}{dt} = g(t) - k_{IC21}N_{20} - k_{ET2}N_{20};$$

$$\frac{dN_{12}}{dt} = k_{IC21}N_{20} - k_{ET1}N_{12} - k_{V2}N_{12};$$

$$\frac{dN_{11}}{dt} = k_{V2}N_{12} - k_{ET1}N_{11} - k_{V1}N_{11};$$

$$\frac{dN_{10}}{dt} = k_{V1}N_{11} - k_{ET1}N_{10} - k_{IC10}N_{10};$$

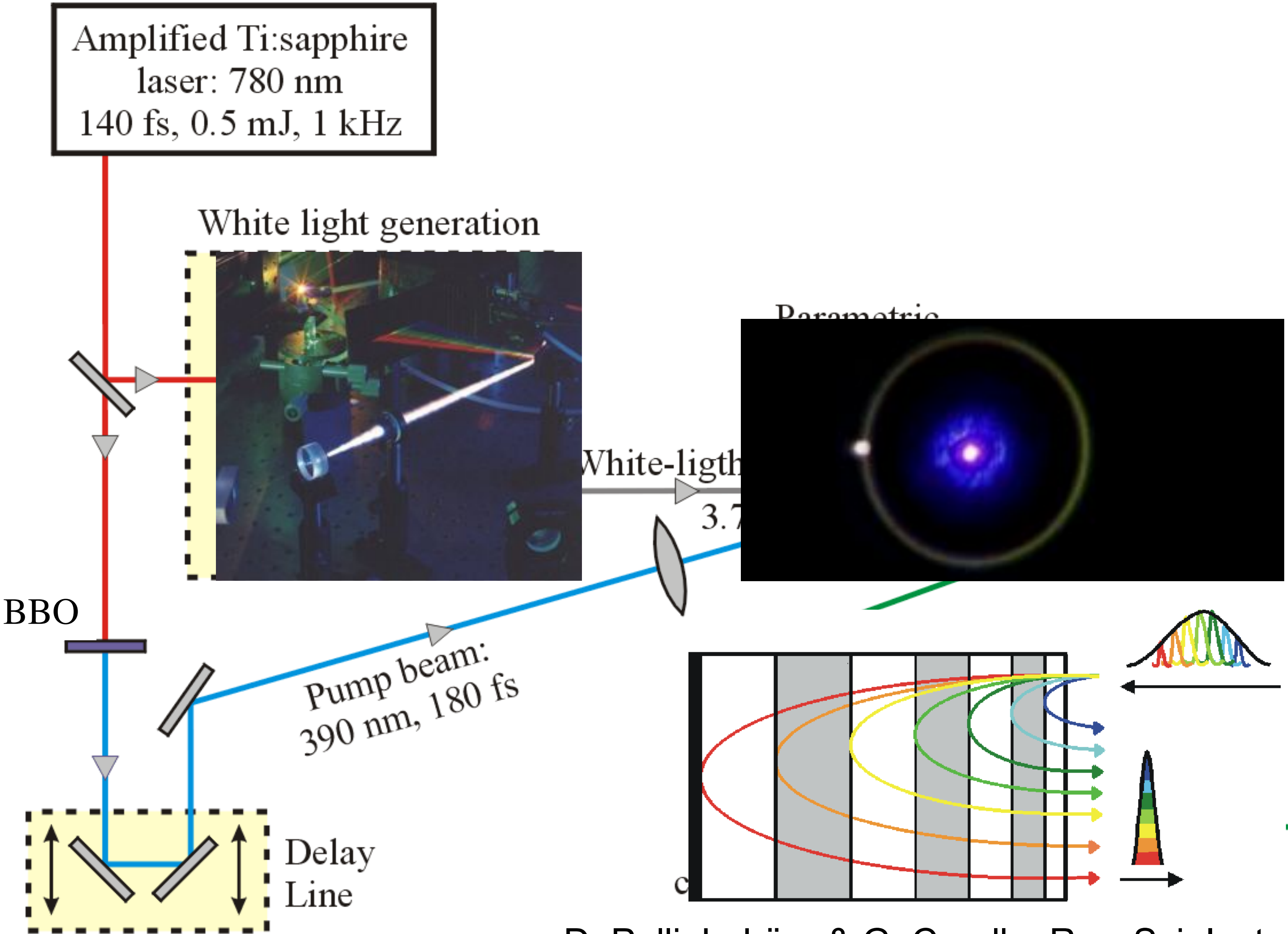
$$\frac{dN_{00}}{dt} = -g(t) + k_{IC10}N_{10} + k_{ET2}N_{20} + k_{ET1}(N_{12} + N_{11} + N_{10}).$$

$$\frac{\Delta T}{T}(\lambda,\tau) = -d\sum_{j=0}^{2}\left[\sigma_{00,2j}(\lambda)\Delta N_{00}(\tau)\right] - d\sum_{i,j=0}^{2}\left[\sigma_{1i,2j}(\lambda)\Delta N_{1i}(\tau)\right] - d\sum_{j=0}^{2}\left[\sigma_{20,0j}(\lambda)\Delta N_{20}(\tau)\right],$$

Results

	Okenone/*C. purpuratum*	Rhodopin glucoside/*R. acidophila*
S_1–S_n energy gap	1.91 eV (Okenone) 2 eV (*C. purpuratum*)	2.12 eV (Rhodopin glucoside) 2.145 eV (*R. acidophila*)
S_1–S_n vibrational energy	110 ± 10 meV	125 ± 10 meV
Gaussian linewidth $\exp\left[-((E - E_0)/\sigma)^2\right]$	σ = 200 ± 12 meV	σ = 63 ± 7 meV
S_1–S_n Huang-Rhys factor γ	0.105 ± 0.005	0.124 ± 0.005
$(k_{IC21})^{-1}$	95 (−5 +8) fs	137 (−11 +10) fs
$(k_{IC10})^{-1}$	4460 (−160 +180) fs	4280 (−190 +160) fs
$(k_{ET2})^{-1}$	55.7 (−6 +2) fs	140 (−15 + 10) fs
$(k_{ET1})^{-1}$	2780 (−110 +270) fs	80,000 ± 10,000 fs

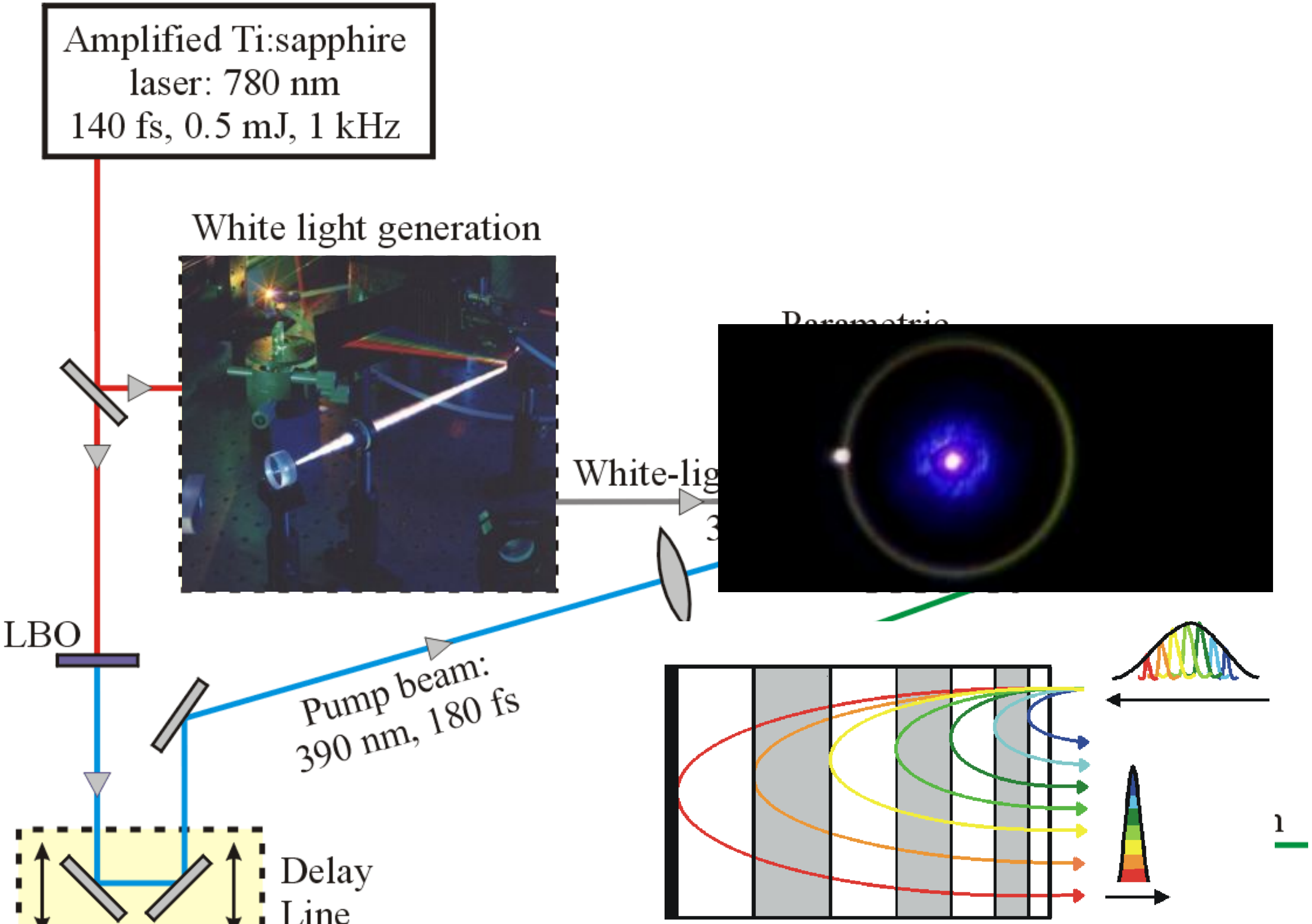
The Visible Non-collinear OPA



$\hbar\omega_1 = \hbar\omega_2 + \hbar\omega_3$
$\hbar k_1 = \hbar k_2 + \hbar k_3$

D. Polli, L. Lüer & G. Cerullo, Rev. Sci. Instrum. **78**, 103108 (2007)

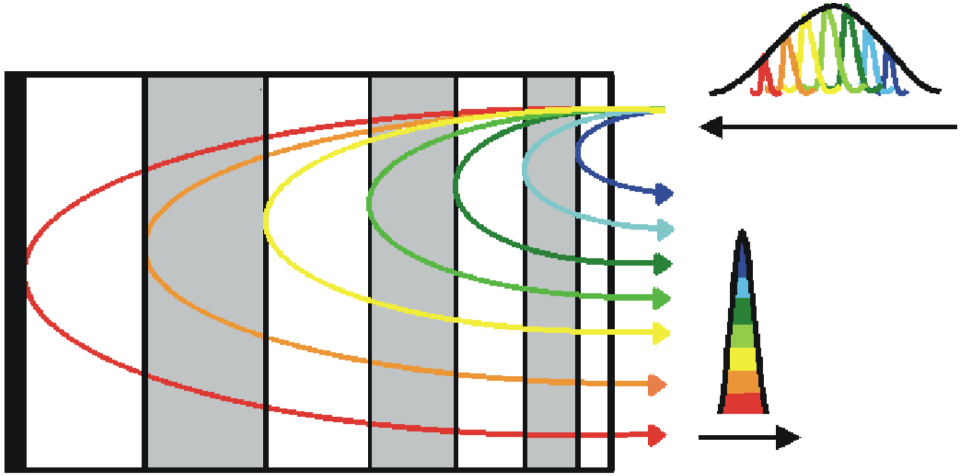
The Visible Non-collinear OPA



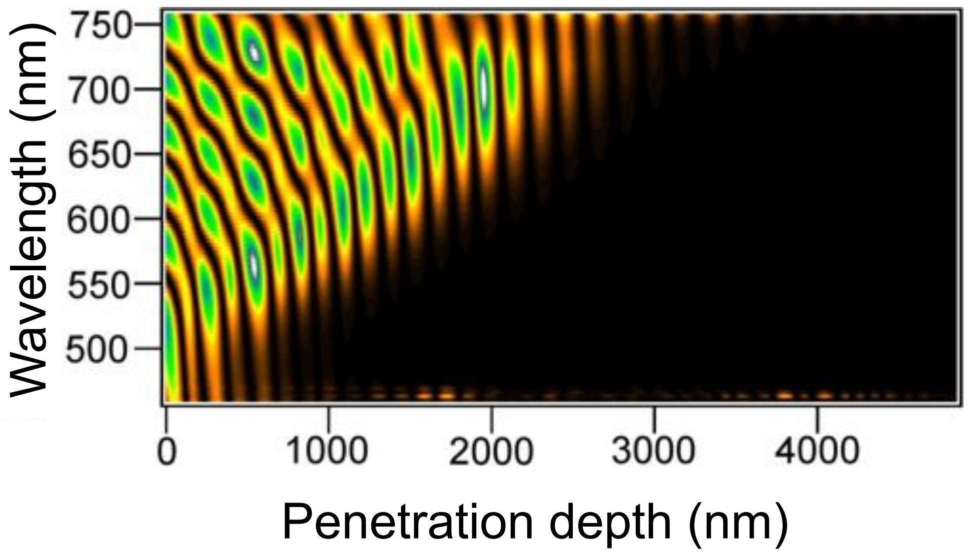
$\hbar\omega_1 = \hbar\omega_2 + \hbar\omega_3$
$\hbar k_1 = \hbar k_2 + \hbar k_3$

A. Shirakawa, et al.,*Appl. Phys. Lett*. **74**, 2268 (1999)
M. Zavelani-Rossi et al., *Opt. Lett*. **26**, 1155 (2001)

Pulse compression with Chirped Mirrors

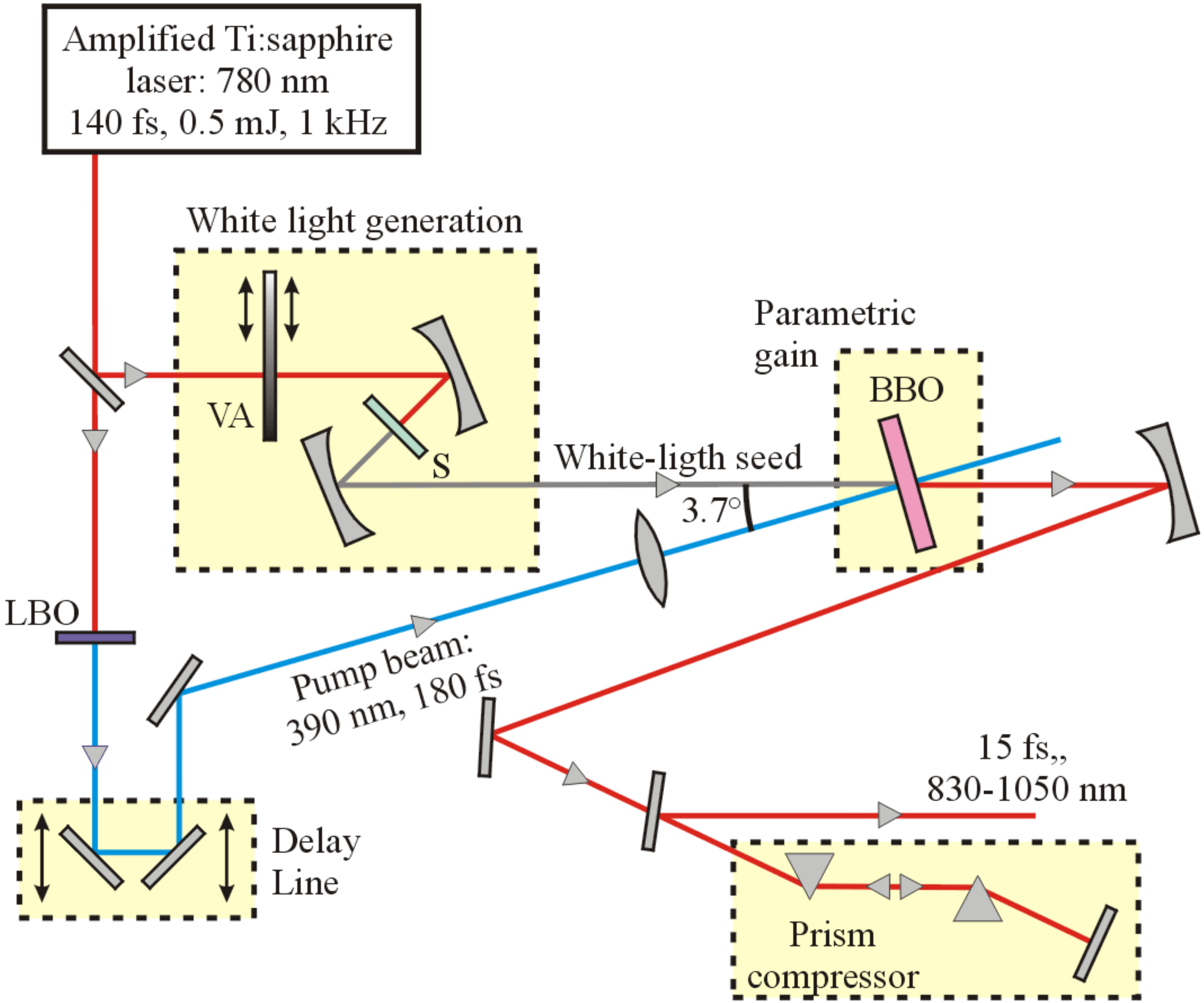


Wavelength-dependent delay ⇒ pulse compression

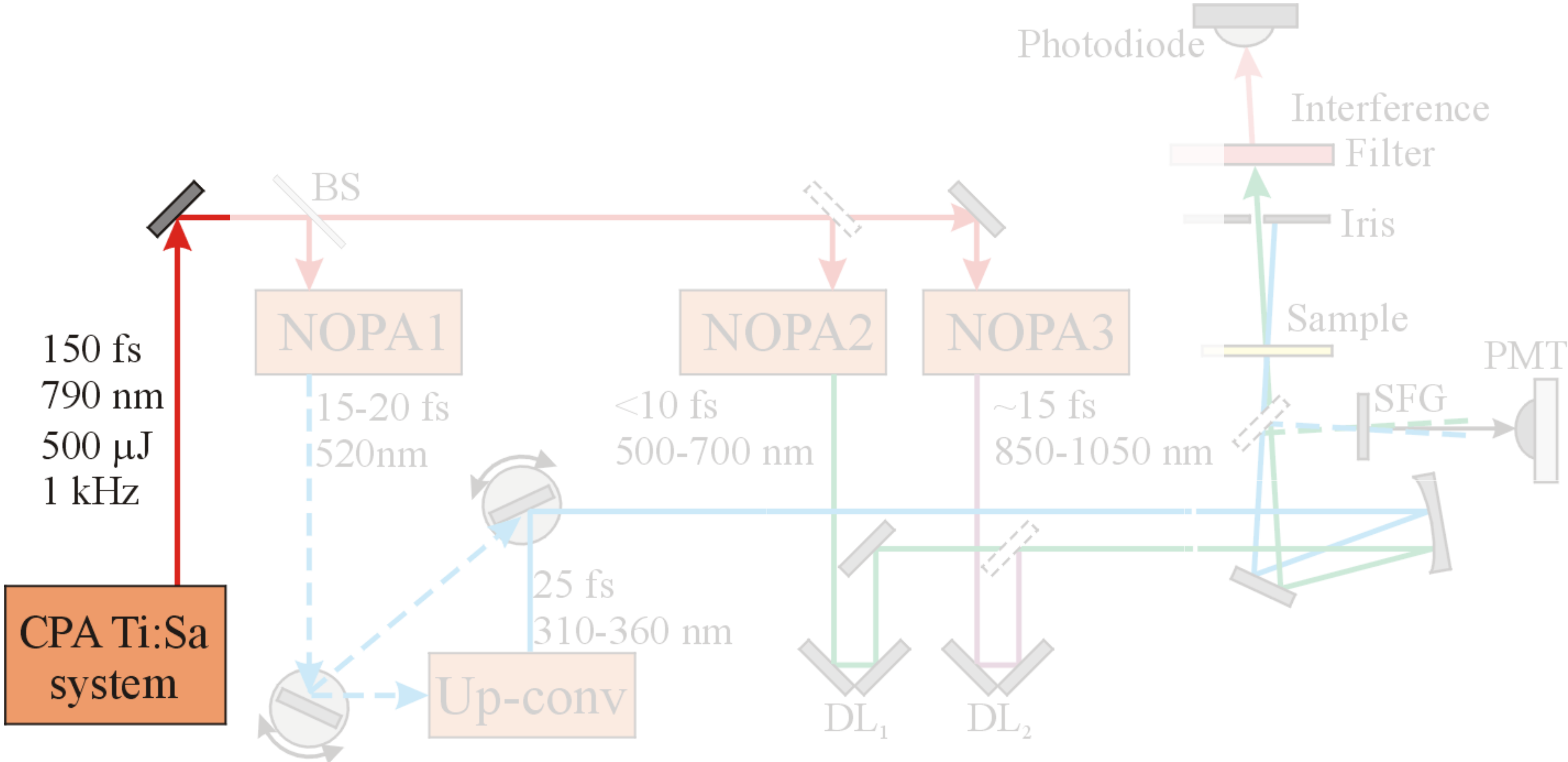


Longer wavelengths penetrate more into depth ⇒ negative dispersion

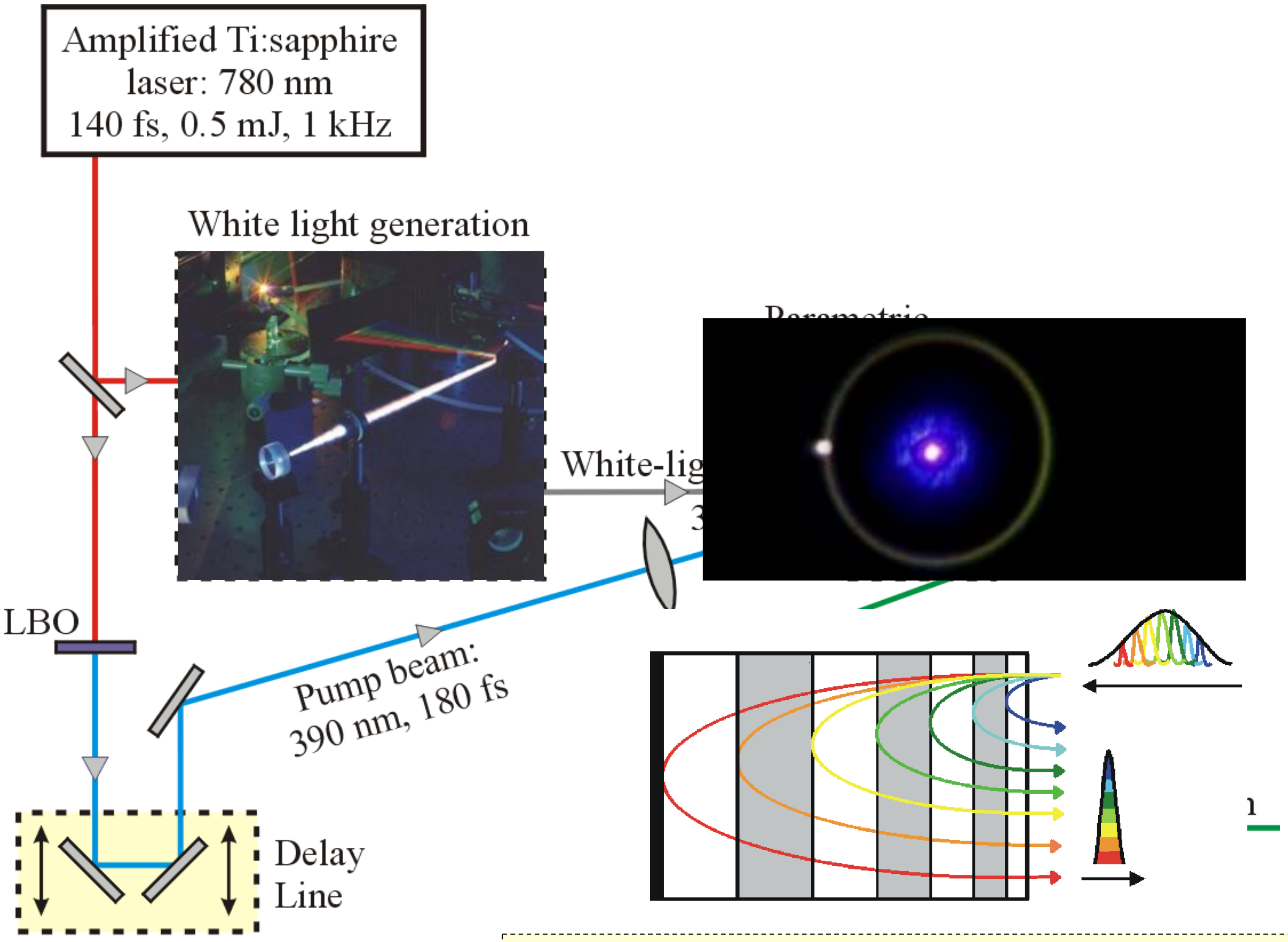
The Near-Infrared Non-collinear OPA



Ultrabroadband Pump-Probe Spectroscopy Setup



The Visible Non-collinear OPA

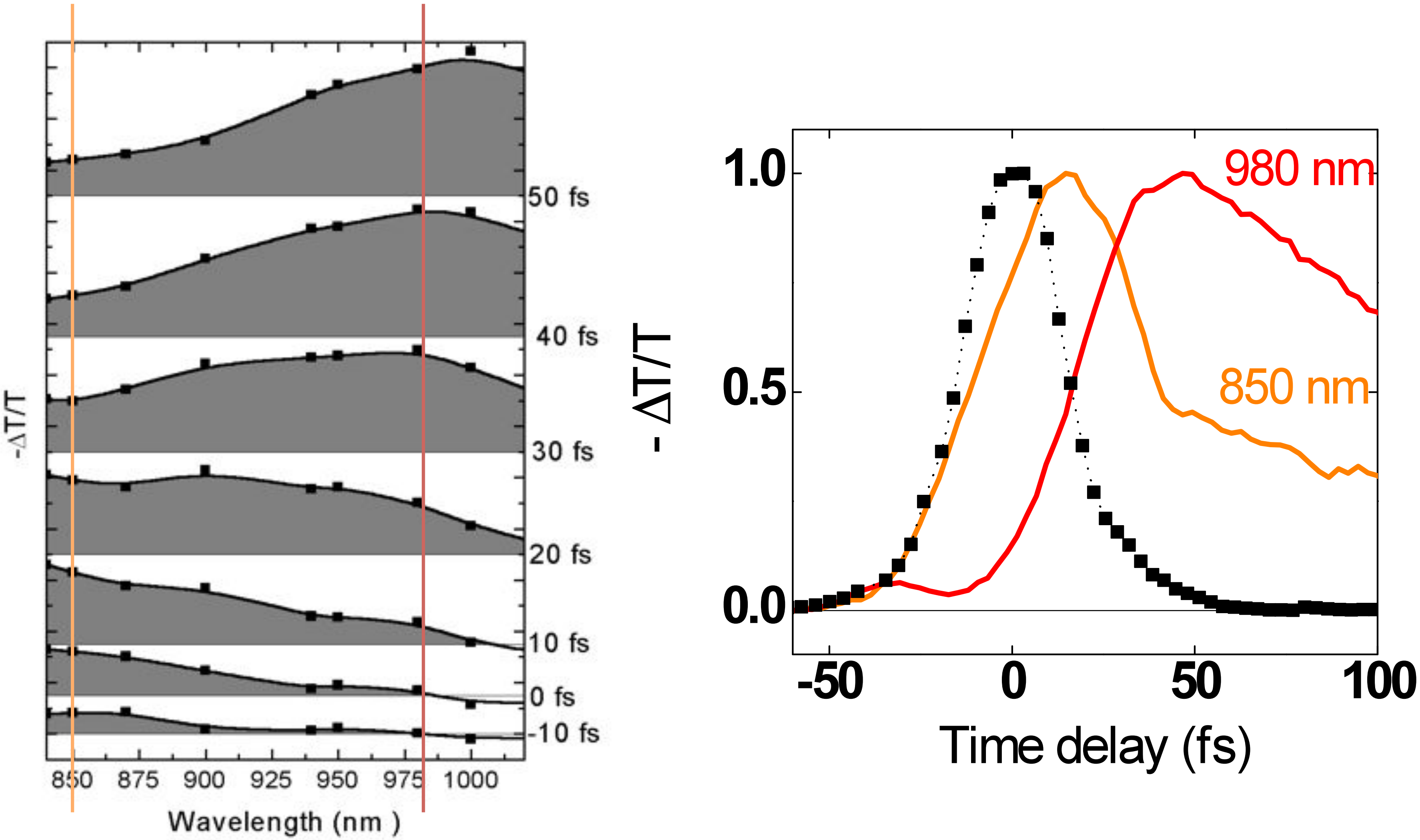


$\hbar\omega_1 = \hbar\omega_2 + \hbar\omega_3$

$\hbar k_1 = \hbar k_2 + \hbar k_3$

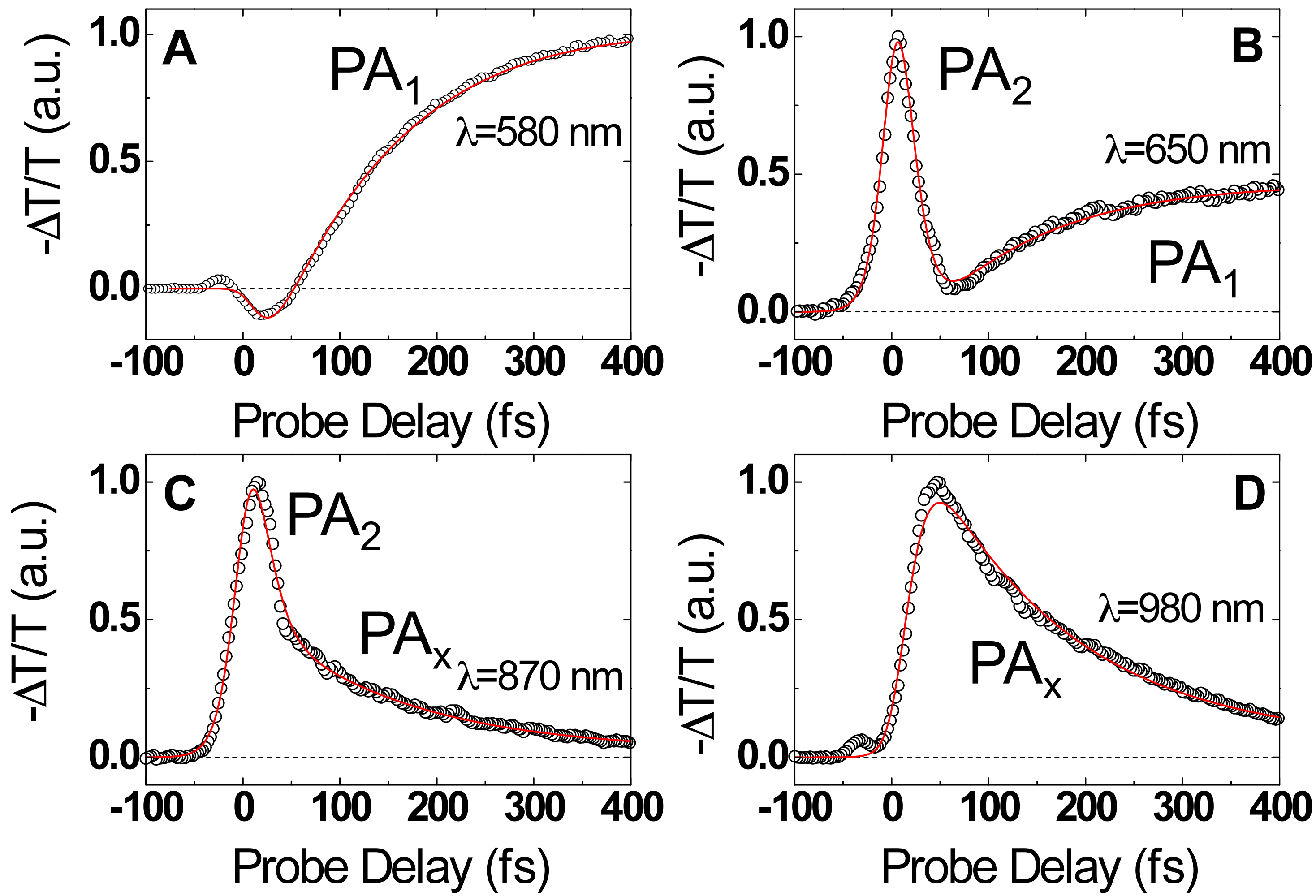
A. Shirakawa, et al.,*Appl. Phys. Lett*. **74**, 2268 (1999)
M. Zavelani-Rossi et al., *Opt. Lett.* **26**, 1155 (2001)

NIR Evolution of the Initial PA in β-carotene



Rapid disappearance of a band and formation of a second red-shifted band

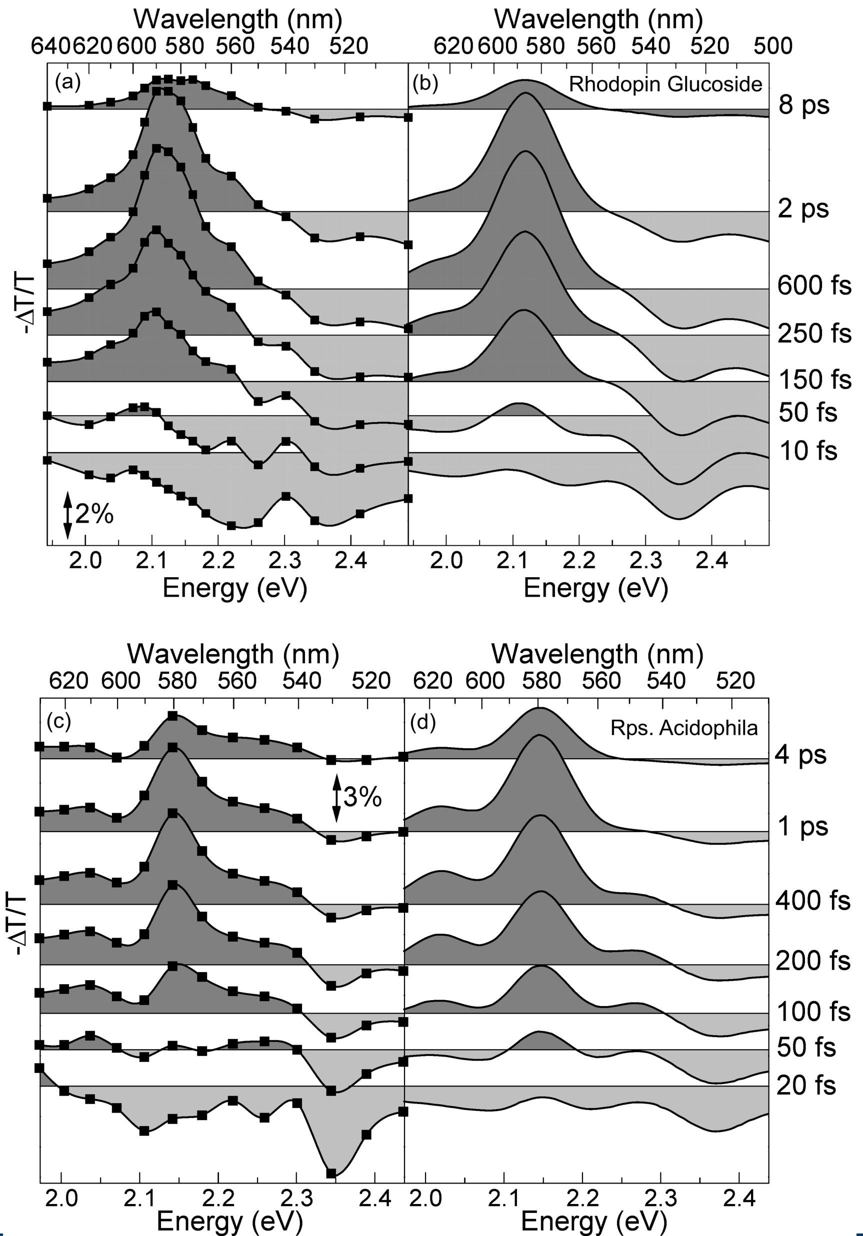
Transmission Difference Dynamics in β-carotene



- Red lines are **fits** using a four-level model
- We extract the time constants **τ_{2x} = 10 fs, τ_{x1} = 150 fs**

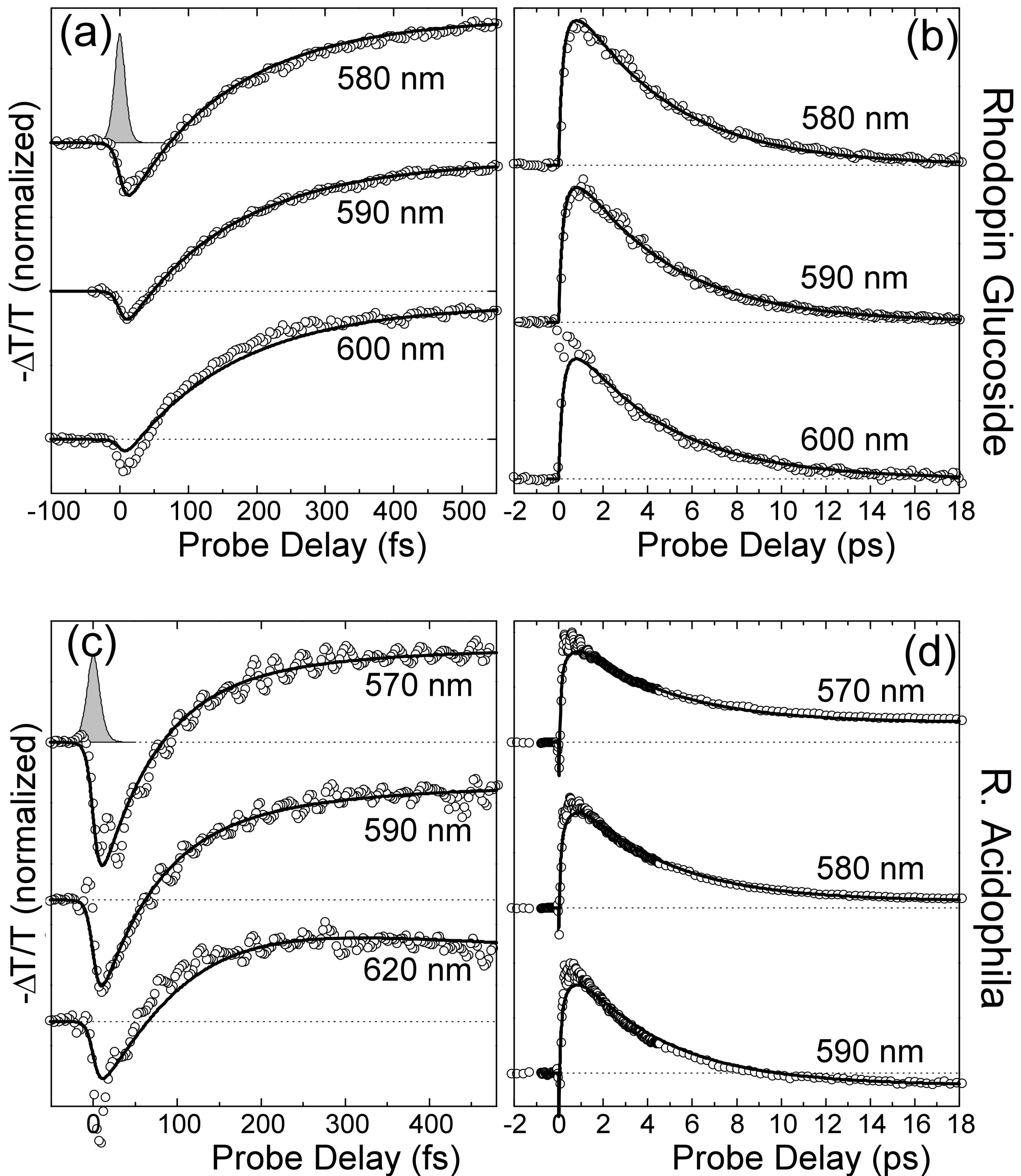
Pump-Probe spectra at various delays

Experimental Results

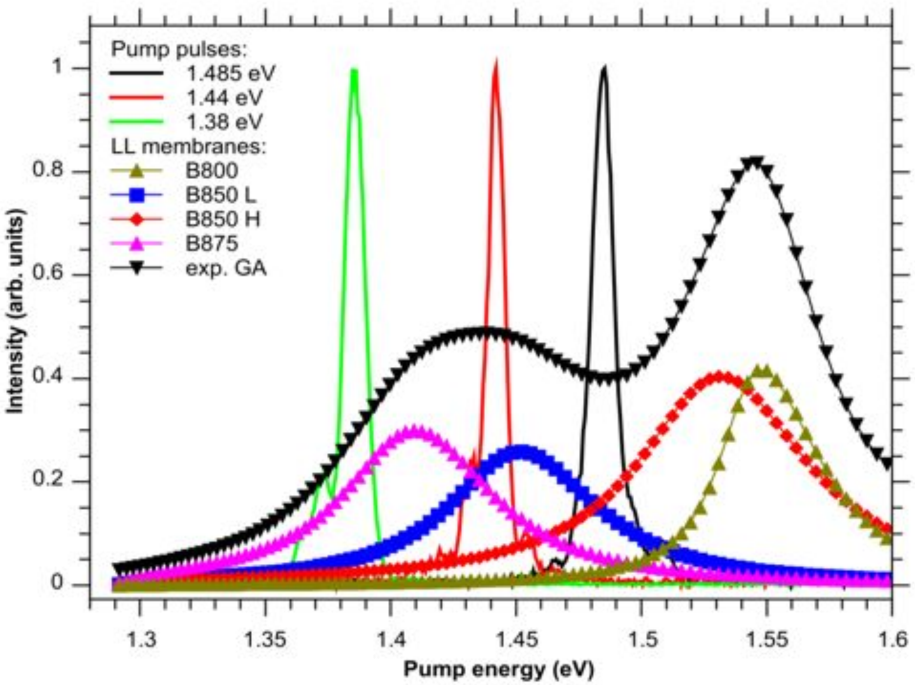


Fits

Pump-Probe dynamics at various probe wavelengths

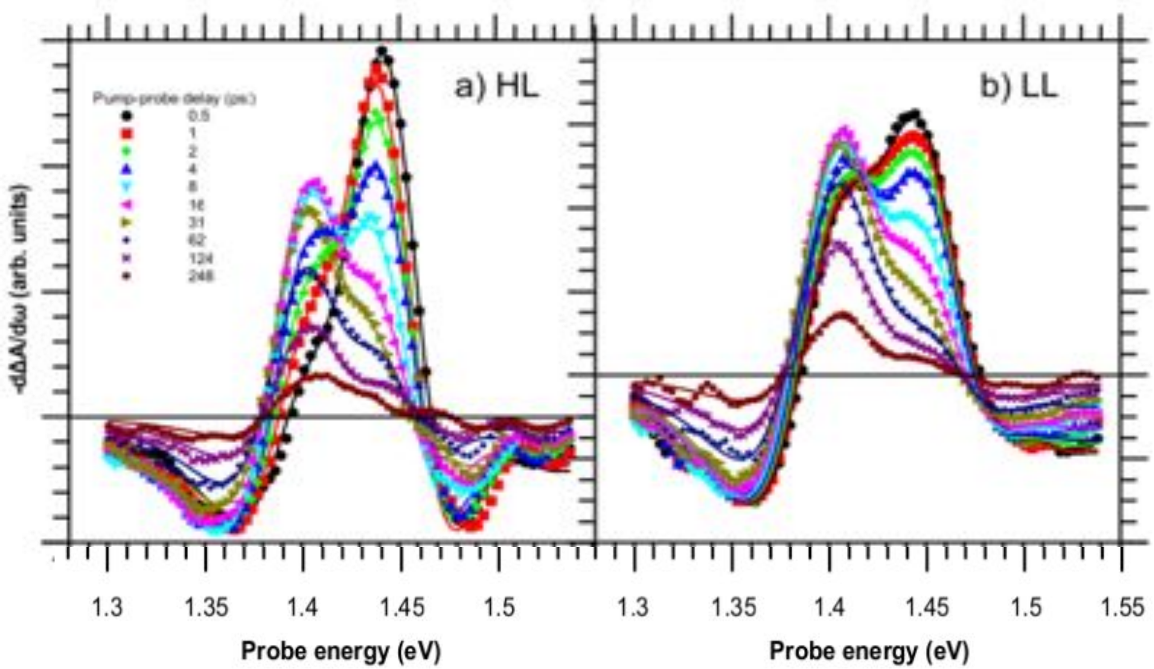


Selective pumping: narrowband OPA



- Pump-probe spectroscopy with tunable pump pulses from 820 to 900 nm.
- Initial ratio r0=B850/(b875+B850) can be varied from 20-80 %.
- Allows to detect equilibration dynamics towards equilibrium.
- Pump intensity as low as possible to limit annihilation

ET rate constants: 1. Time-dependent populations



E(pu)=1.48 eV
Closed RC

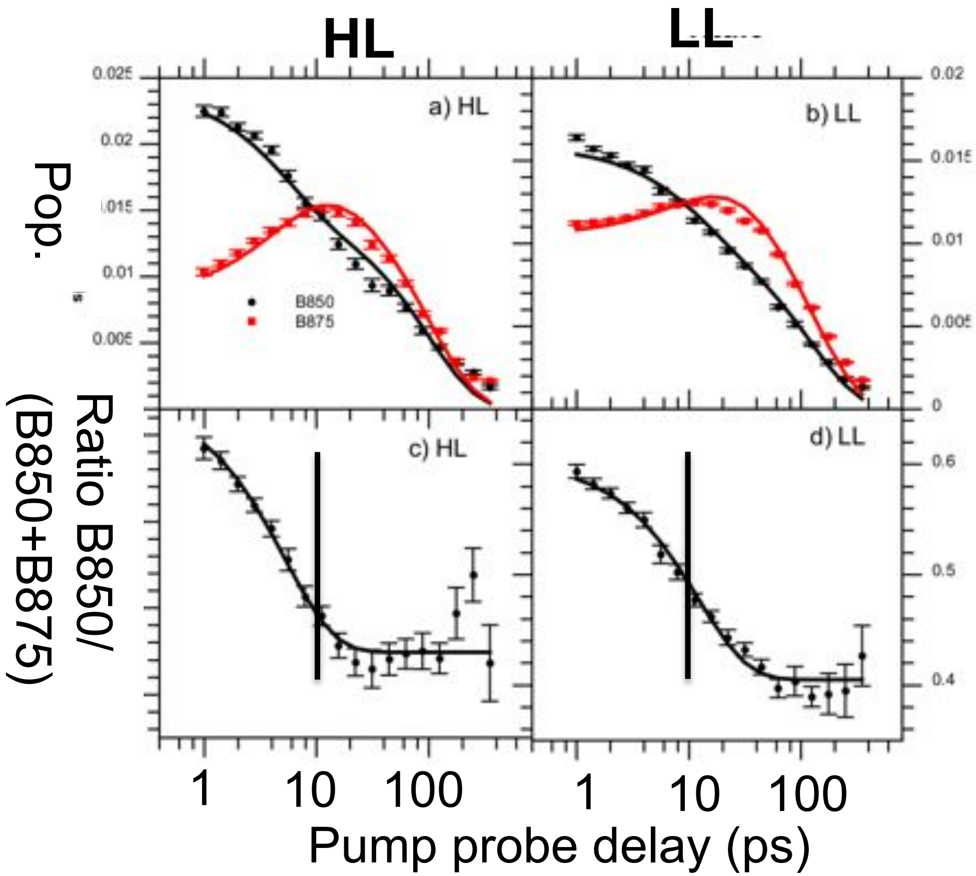
Cross-sections not time-dependent
Same cross-sections for B850 and B875 →
Spectral widths can be directly associated with ***populations***

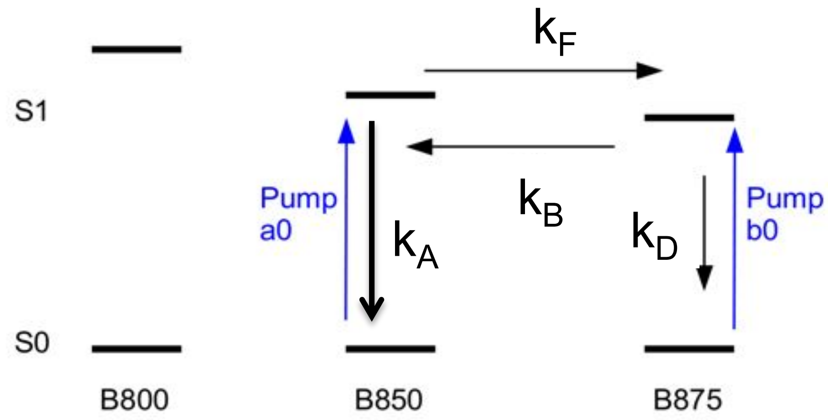
- **Two-step procedure:**

–Fit 3 second derivatives of Voigt profiles
–Free parameters: (weight / width /center) for each Voigt band
- The widths did not show significant variation with time

–Repeat fits with fixed weights
- Result: virtually no significant deviations → populations useful for kinetic modeling

ET rate constants



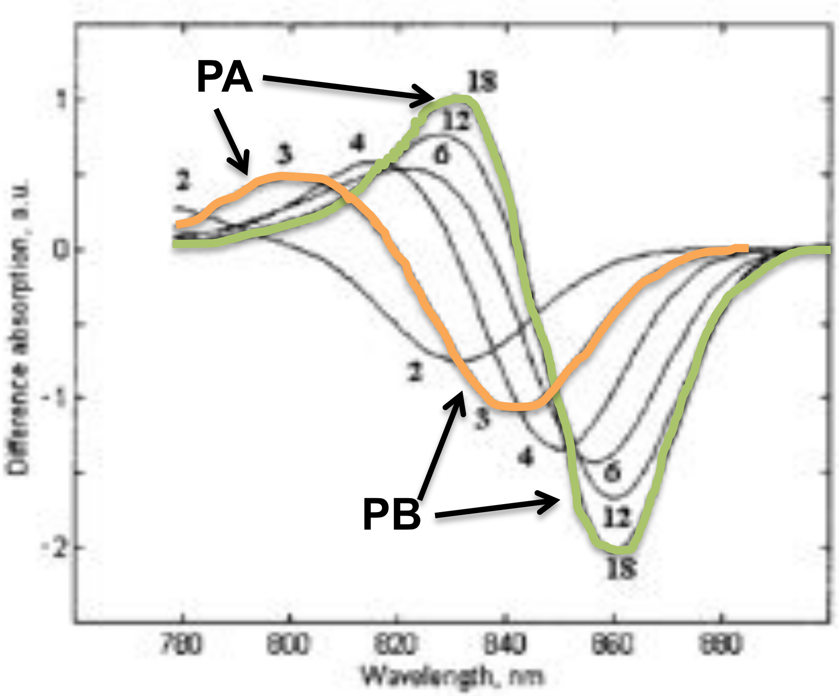


Model has analytical solution
Predictions for r=B850(B850+B875):
Equilibration dynamics ~ kF+kB
Equilibrium ~ kF/(kF+k2B)

- Model describes populations from first fit very well
- First order equilibration dynamics, followed by true equilibrium
- KF and kB will be reliable
- System behaves as a homogeneous reaction

Lüer *et al.*, *PNAS* **109**, 1473 (2012)

PA and PB bands in LH complexes



Calculated TA spectrum of B850 fragment

- Calculations of TA spectra in B850 fragments show PA blue-shifted against PB. (*Novoderezhkin, Monshouwer, van Grondelle, J. Phys. Chem. B, Vol. 103, No. 47, 1999*)
- Shift of PA against PB depends on N
- For N>6, it becomes so small that first-derivative shape is observed

Samples

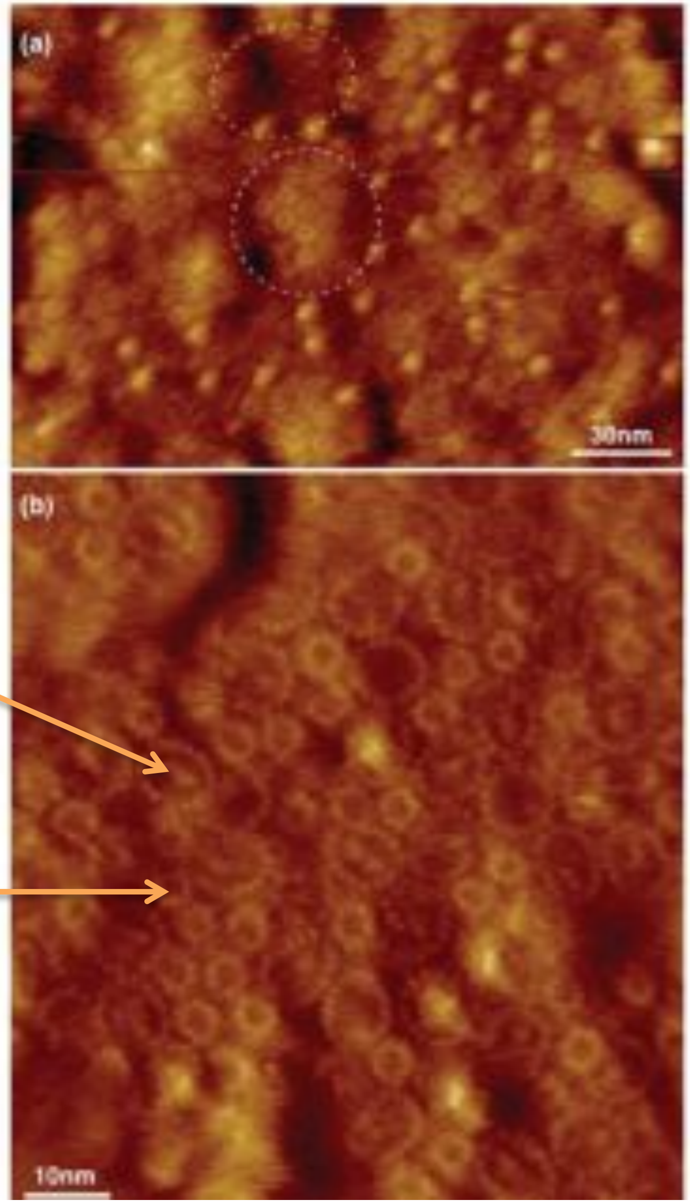
Photosynthetic membranes of

Rhodopseudomonas palustris

- Grown under high and low light conditions (**HL** (220 lux) and **LL**(10 lux; sun > 30000 lux))

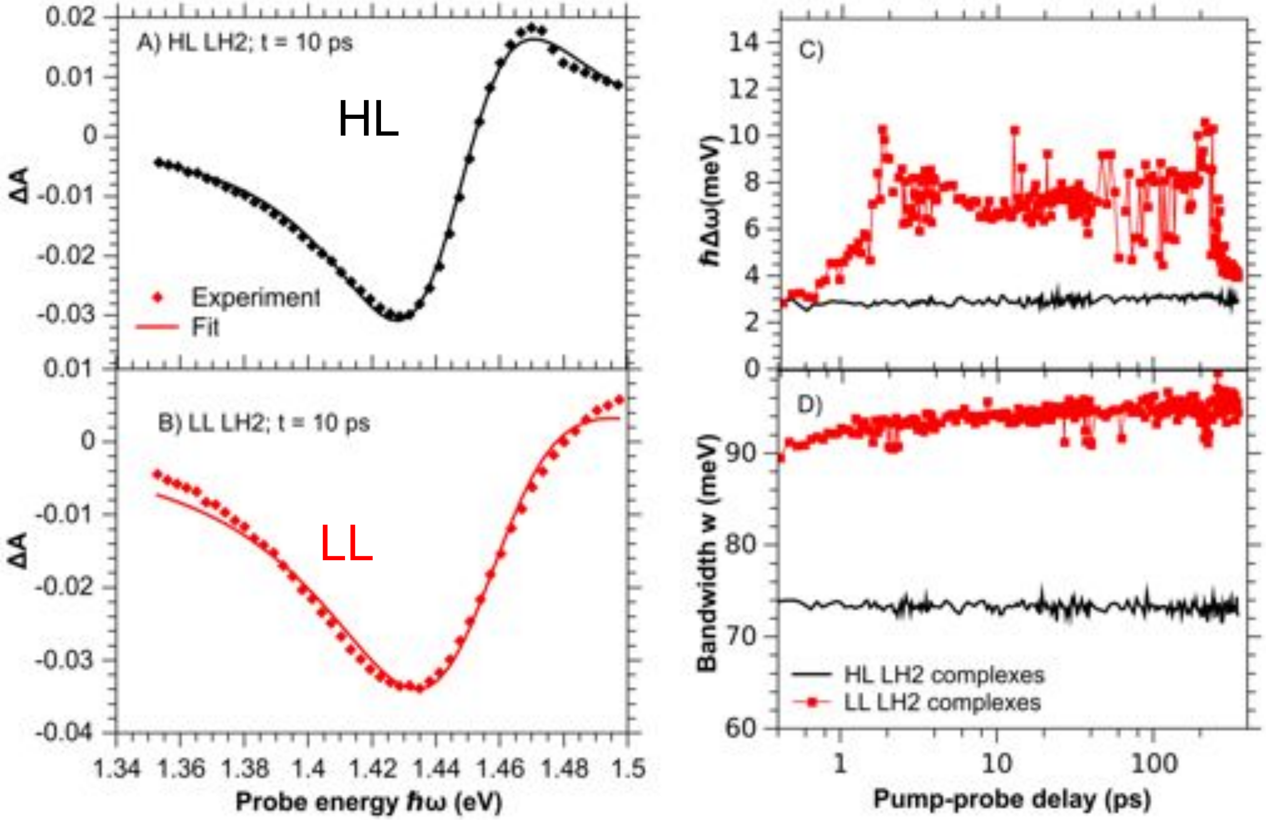
- With open and closed reaction centers (done at Glasgow University)

- LH2:LH1 ratio:
  - 1:1 in HL, 2:1 in LL



Scheuring *et al., J. Mol. Biol* **358**, 83 (2006)

Fitting of TA spectra

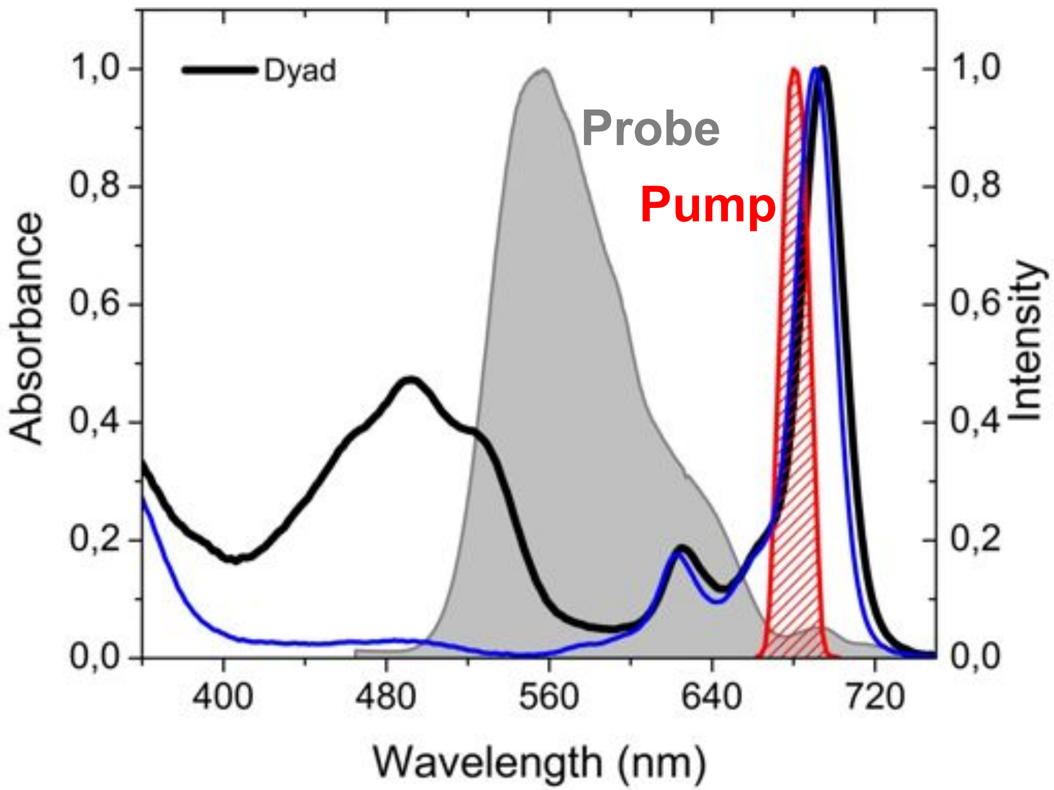


Offset (PA-PB)

Width (PA-PB)

- B850 from LH2 complexes can be fit very well by **two Lorentzians**
- Both have **same width** and **amplitude** for t > 2ps
- **Constant offset**, which is only 1/10 of width for t> 2ps
- TA spectra can be very well approximated by **first derivatives!**

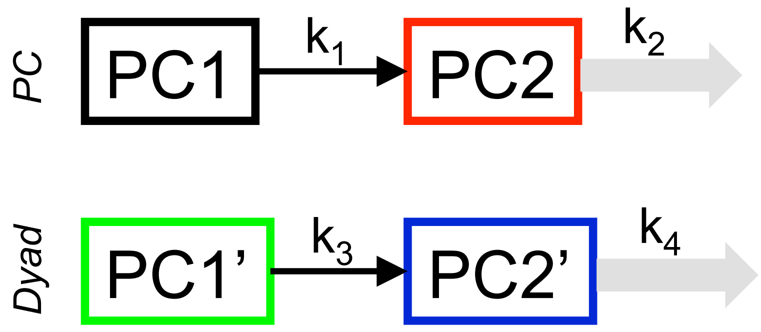
Experimental Results (II)



1. Exciting the Dyad resonant with Car (530 nm)

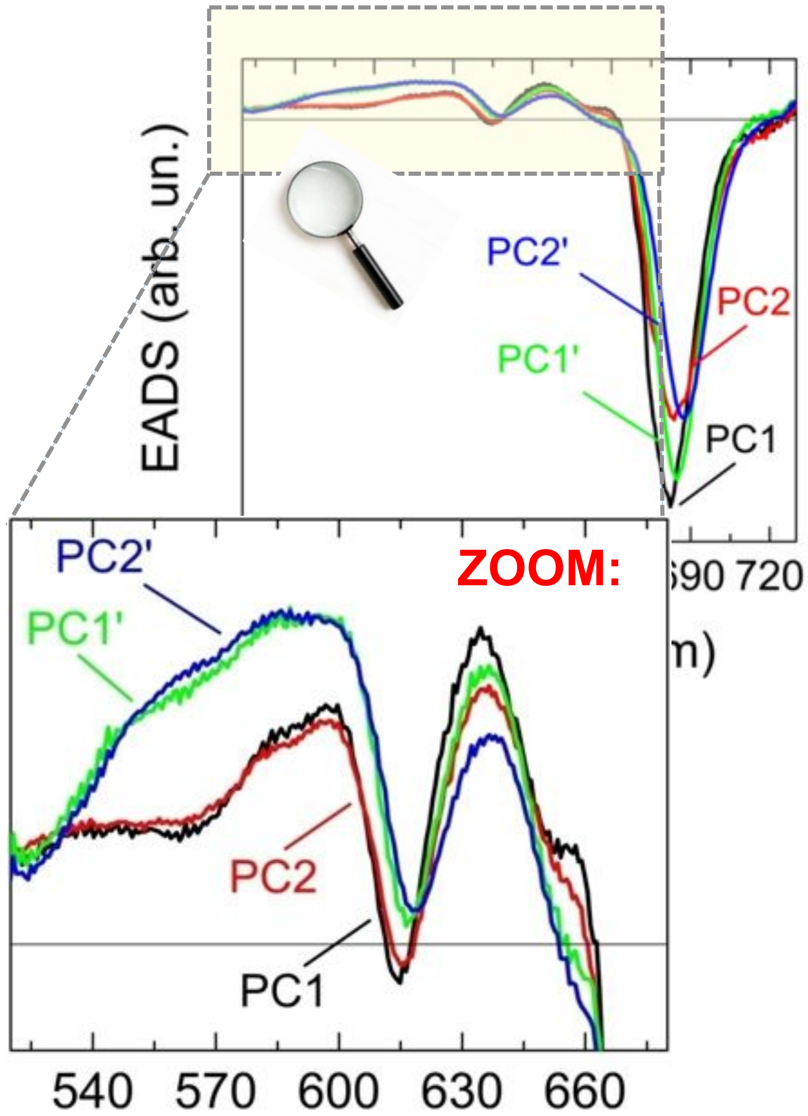
2. Exciting the Dyad resonant with PC (680 nm)

Simple sequential models:

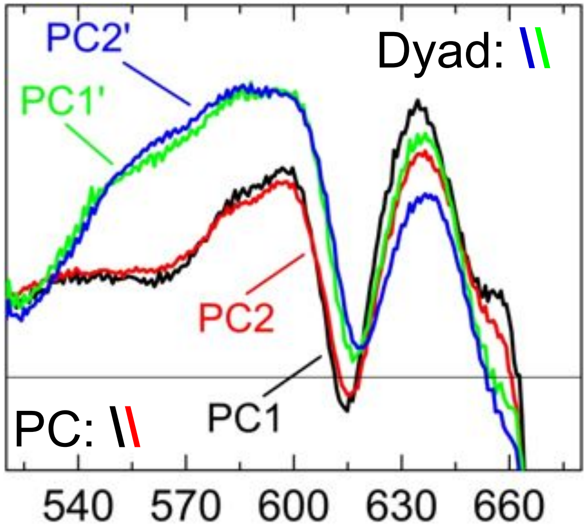


• Discrepancy between EADS estimated from Dyad excitation and EADS from PC only excitation

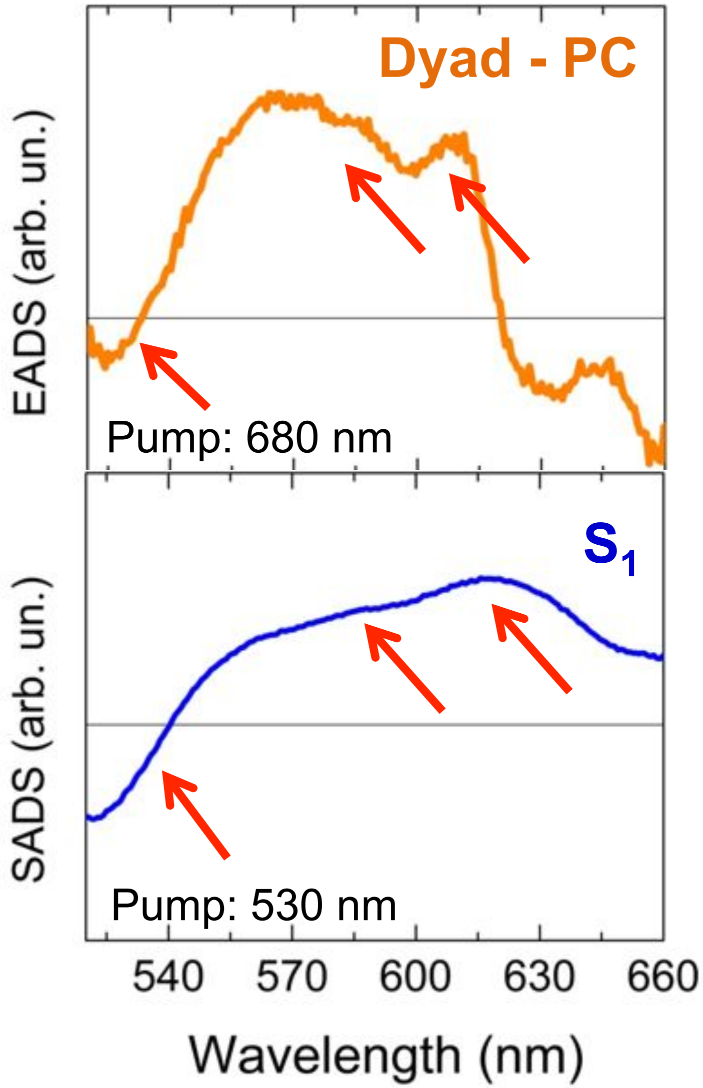
• Appears within the time duration of the IRF (77 fs)



Exciting the PC



Subtract PC EADS from Dyad EADS :



Compare the estimated EADS at **680 nm-pump** with the SADS obtained from the analysis at **530 nm-pump**:

Hint of **S_1 feature-like** when excite the PC in the dyad:

Excitonic Coupling PC-S_1

Conclusions

- **Energy Transfer**

• **Excitonic Coupling Between**

λ Simultaneous global or target analysis allows for full characterization of energy transfer kinetics

λ Strong evidence for the presence of S1 signature upon excitation of Dyad at 680 ndicating excitonic coupling.

Mid-19th century painting

"A Steeplechase" by Carl Frederic Aagaard

Flash photography: “freezing in” motion

Is there a time in the galloping horse´s motion when no hooves are touching the ground? Yes (flash photography, Eadweard Muybridge, 1878, 10^{-3} sec resolution)

Flash photography: “freezing in” motion

He placed numerous large glass-plate cameras in a line along the edge of the track; the shutter of each was triggered by a thread as the horse passed. The path was lined with cloth sheets to reflect as much light as possible.

Flash photography: “freezing in” motion

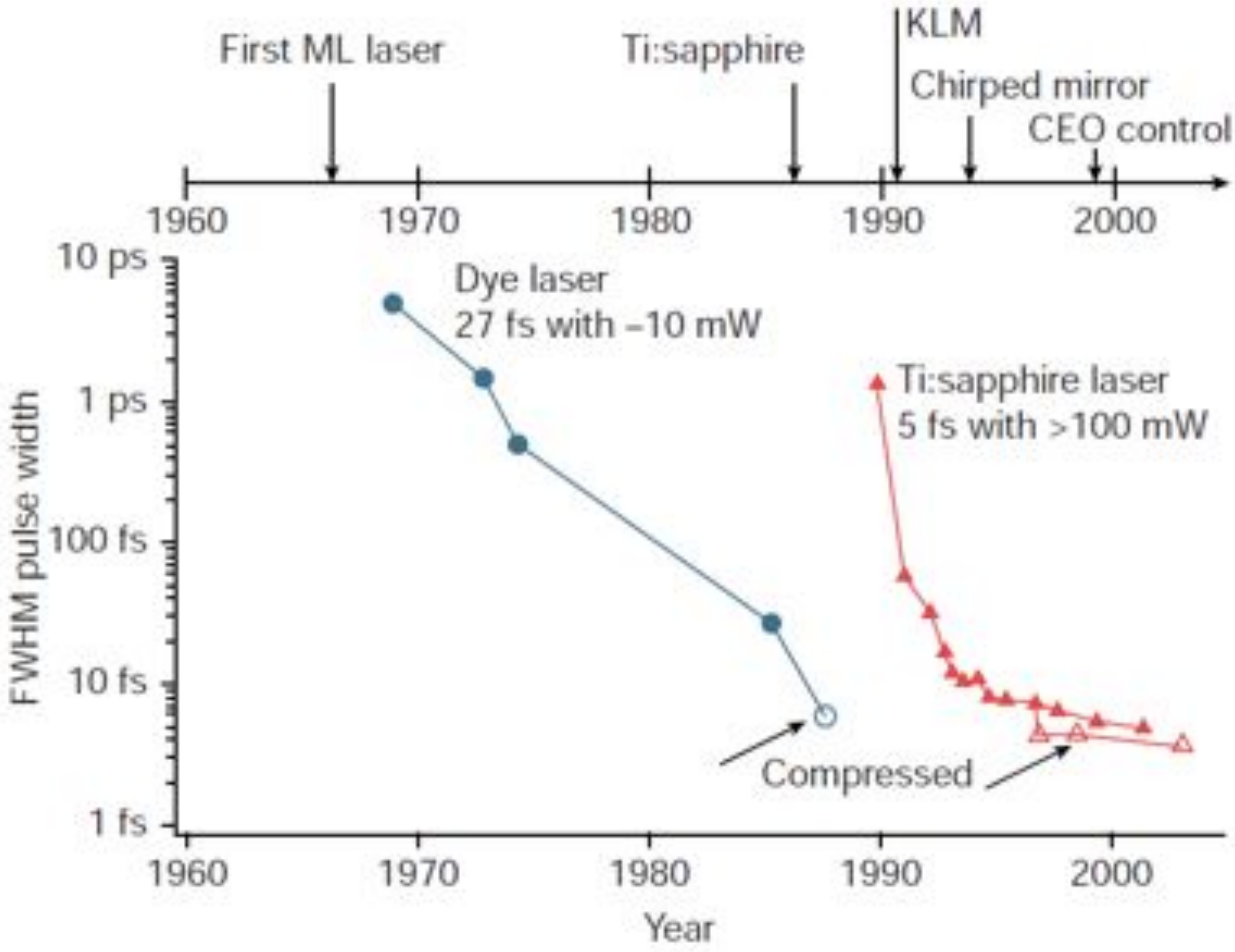
brief communications

Are fast-moving elephants really running?

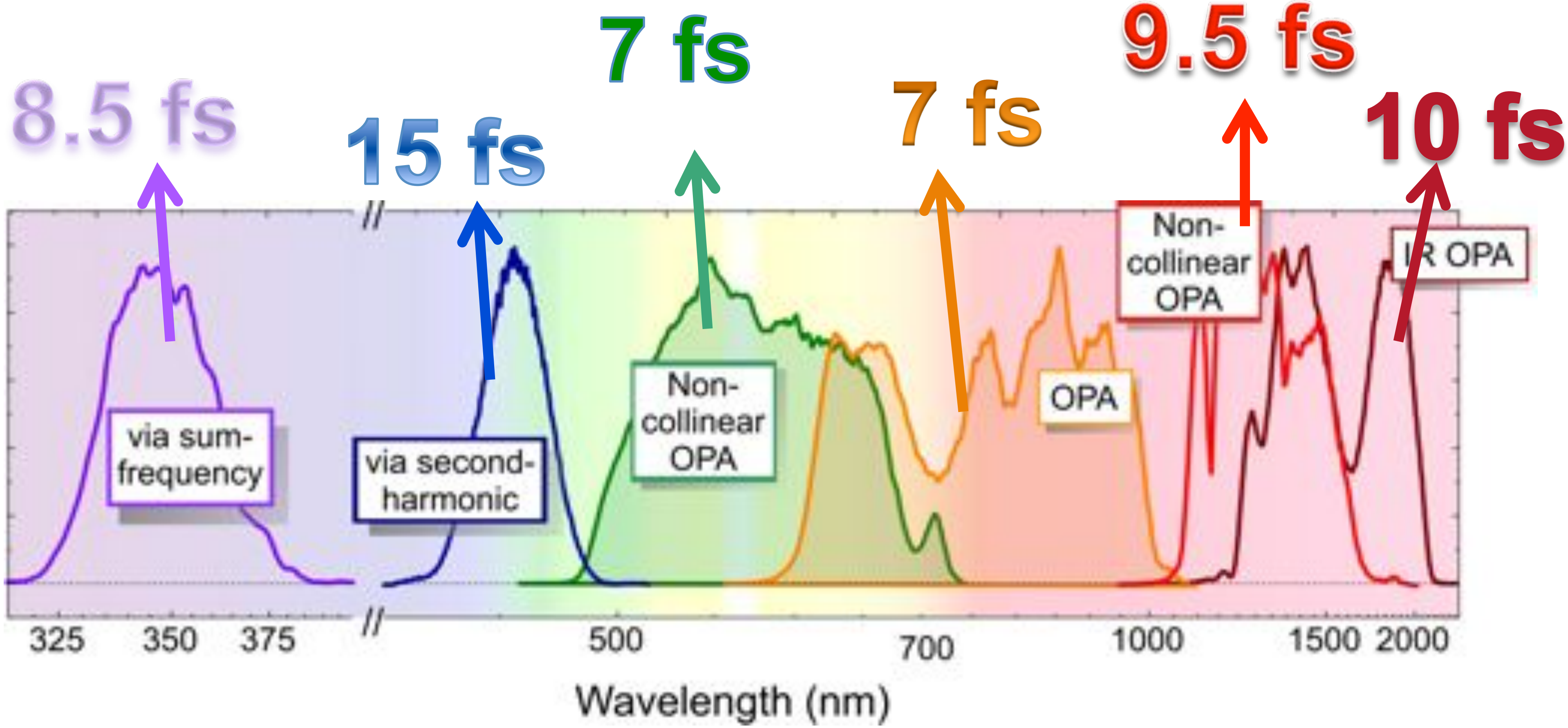
Despite their unseemly bulk, elephants can hit high speeds — but use an unusual style.

No aerial phase!

Then the laser came…

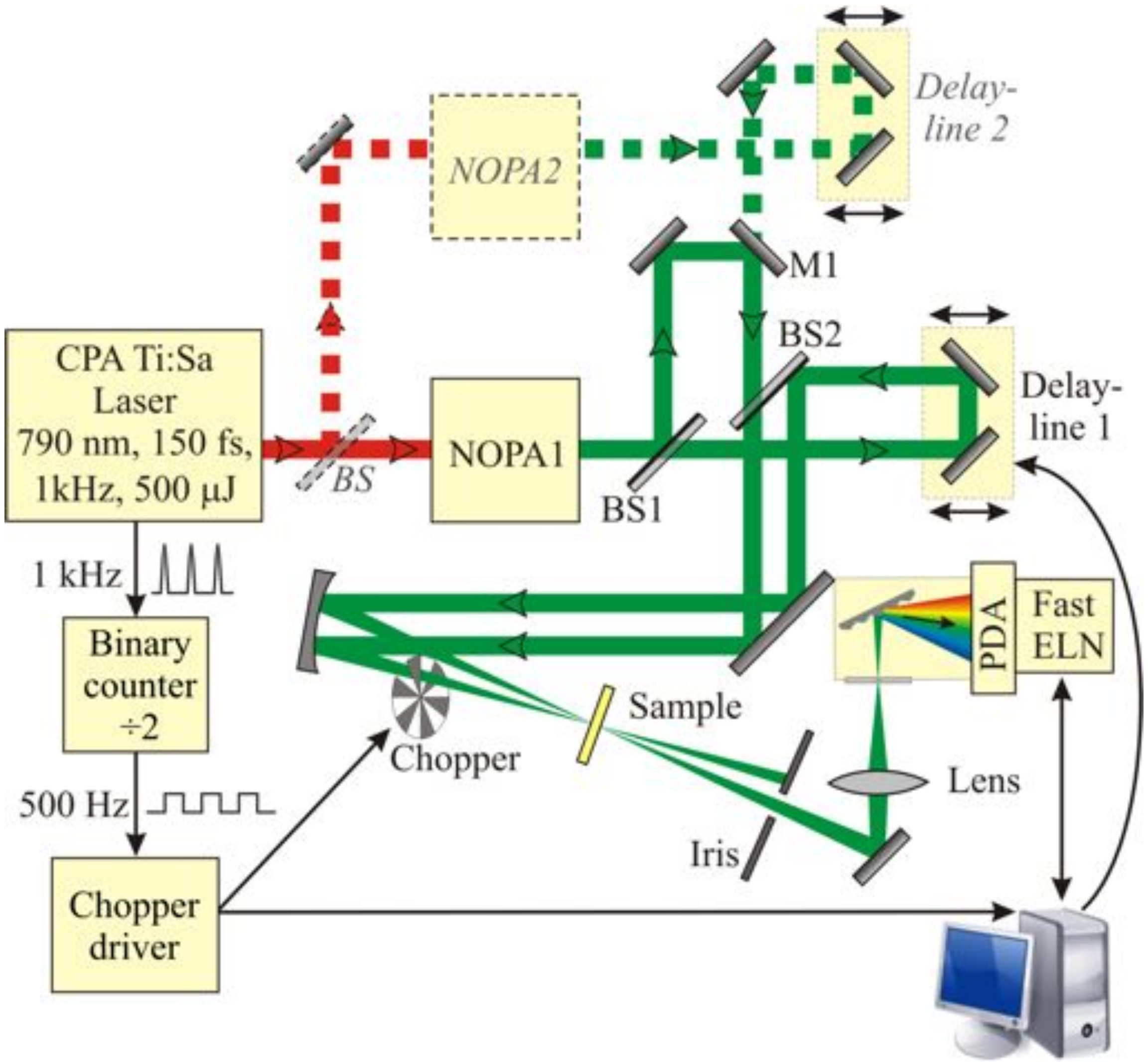


Ultrabroadband Pulse Generation



D. Brida, C. Manzoni, G. Cirmi, D. Polli, and G. Cerullo, IEEE J. Sel. Top. Q. Electron. **18**, 329 (2011).

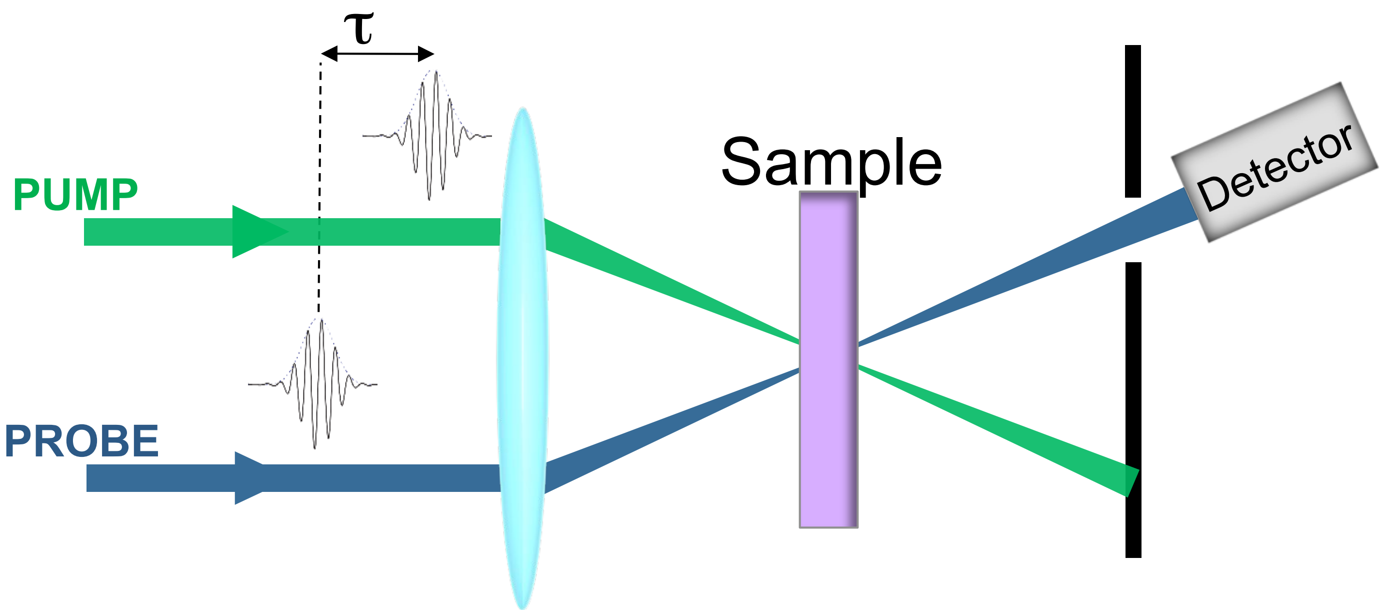
Experimental set-up



D. Polli, L. Lüer & G. Cerullo, Rev. Sci. Instrum. **78**, 103108 (2007)

C. Manzoni, D. Polli and G. Cerullo, Rev. Sci. Instr. **77**, 023103 (2006)

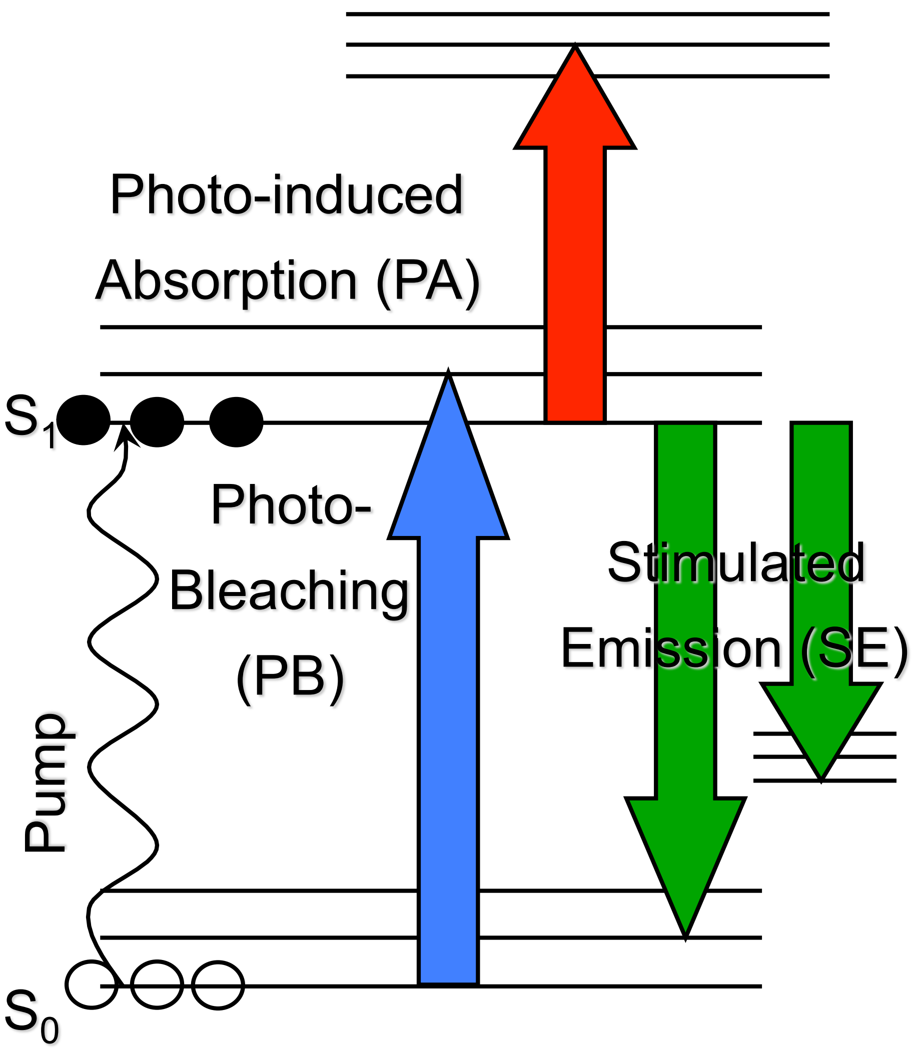
The "pump-probe" technique



- A first **pump** pulse resonantly excites the system
- A second, delayed **probe** pulse detects the pump-induced differential transmission changes:

$$\frac{\Delta T}{T} = \frac{T_{ON}(\lambda_{pr},\tau) - T_{OFF}(\lambda_{pr},\tau)}{T_{OFF}(\lambda_{pr},\tau)}$$

Pump-Probe Signals



Photobleaching (PB):

less molecules in the ground state

⇒ increased transmission $\Delta T/T>0$

Stimulated emission (SE):

from molecules in the excited state

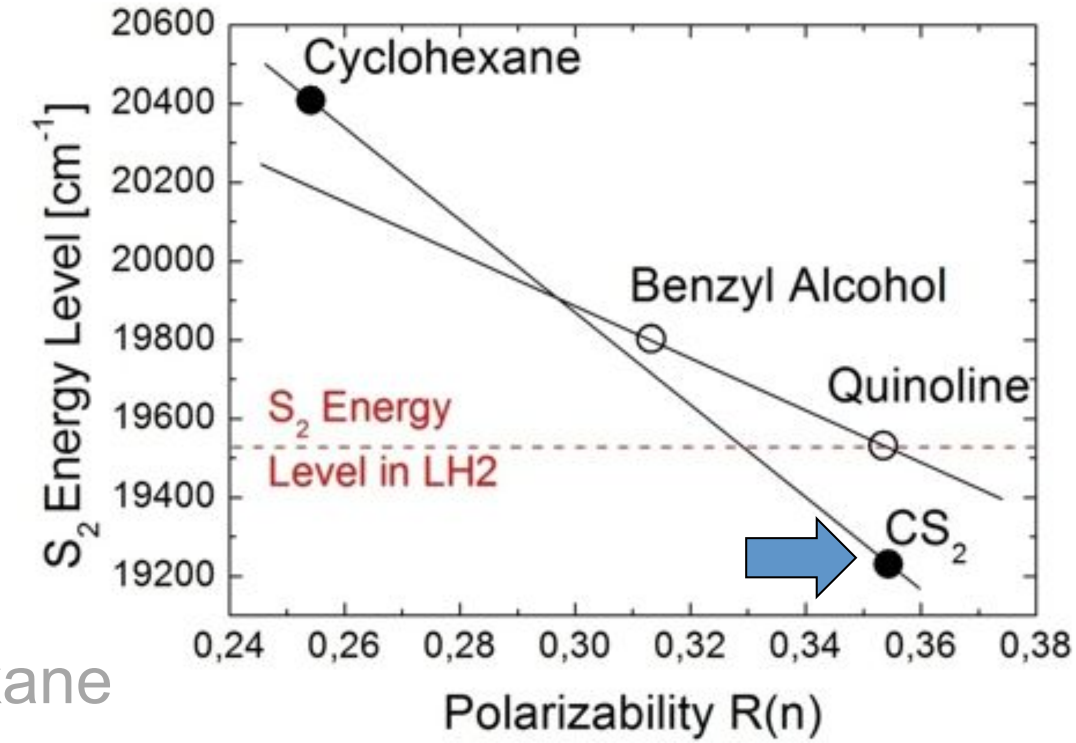
⇒ increased transmission (gain in the sample) $\Delta T/T>0$

Photoinduced absorption (PA):

from excited state to higher states

⇒ decreased transmission $\Delta T/T<0$

Experimental Results (I)

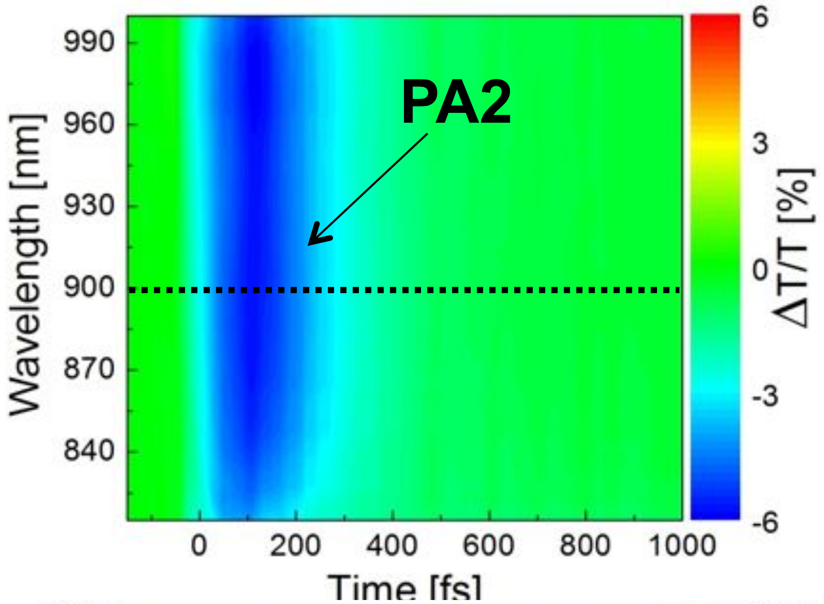


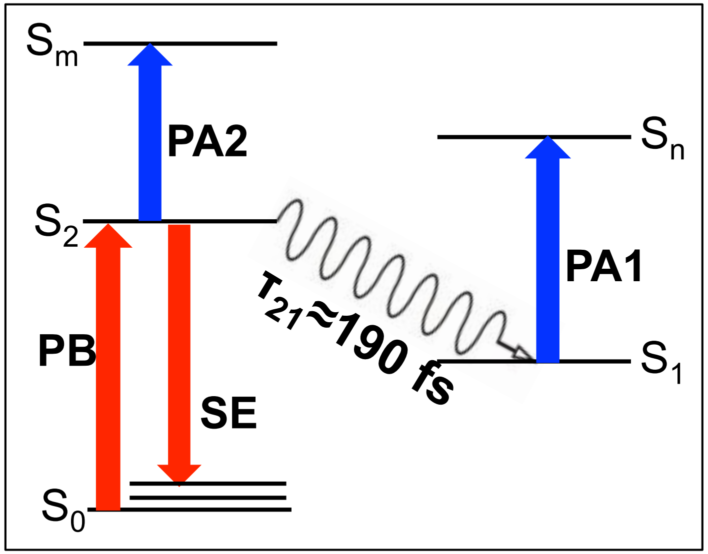
1. Spheroidene in CS_2

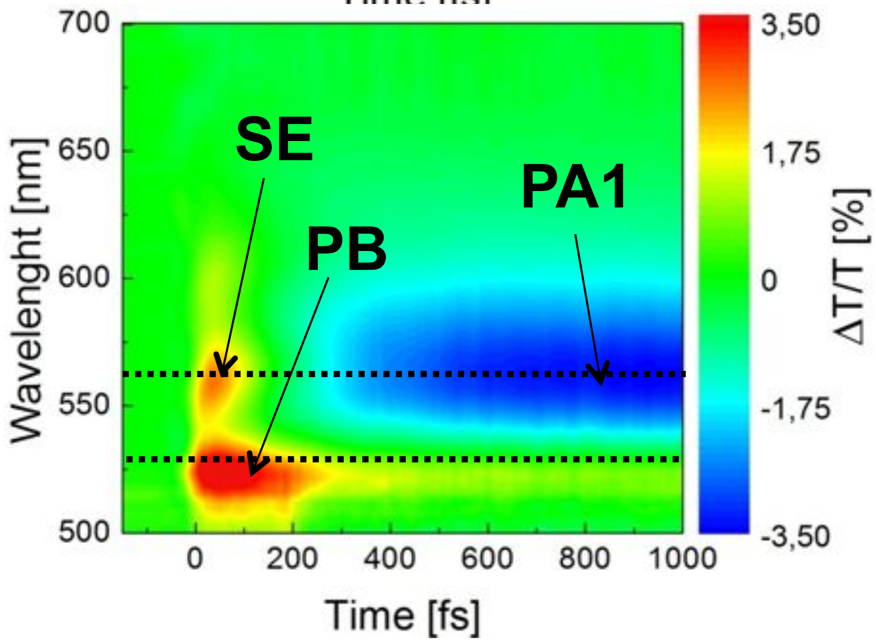
2. Spheroidene in Cyclohexane

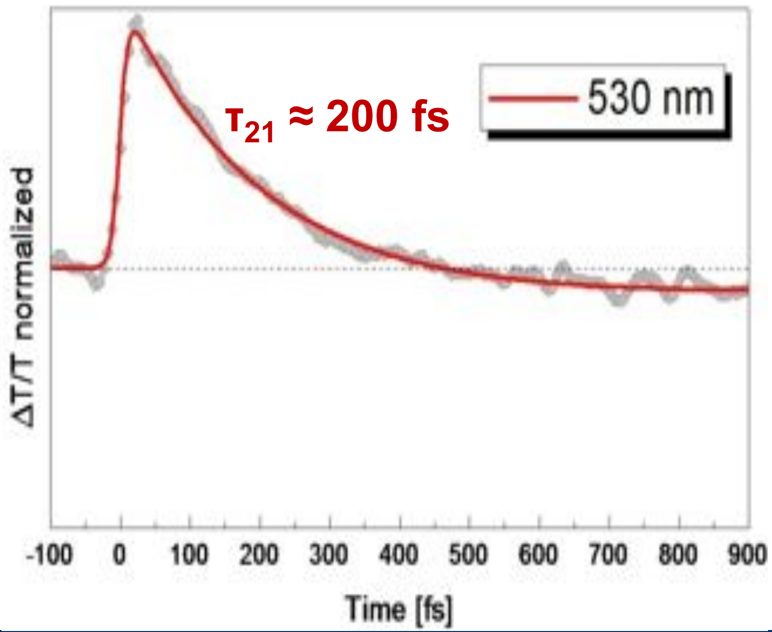
M. Maiuri, D. Polli, D. Brida, L. Lüer, A. M. LaFountain, M. Fuciman, R. J. Cogdell, H. A. Frank, and G. Cerullo, *Phys. Chem. Chem. Phys*. **14**, 6312-6319 (2012).

Internal Conversion of Spheroidene in CS_2





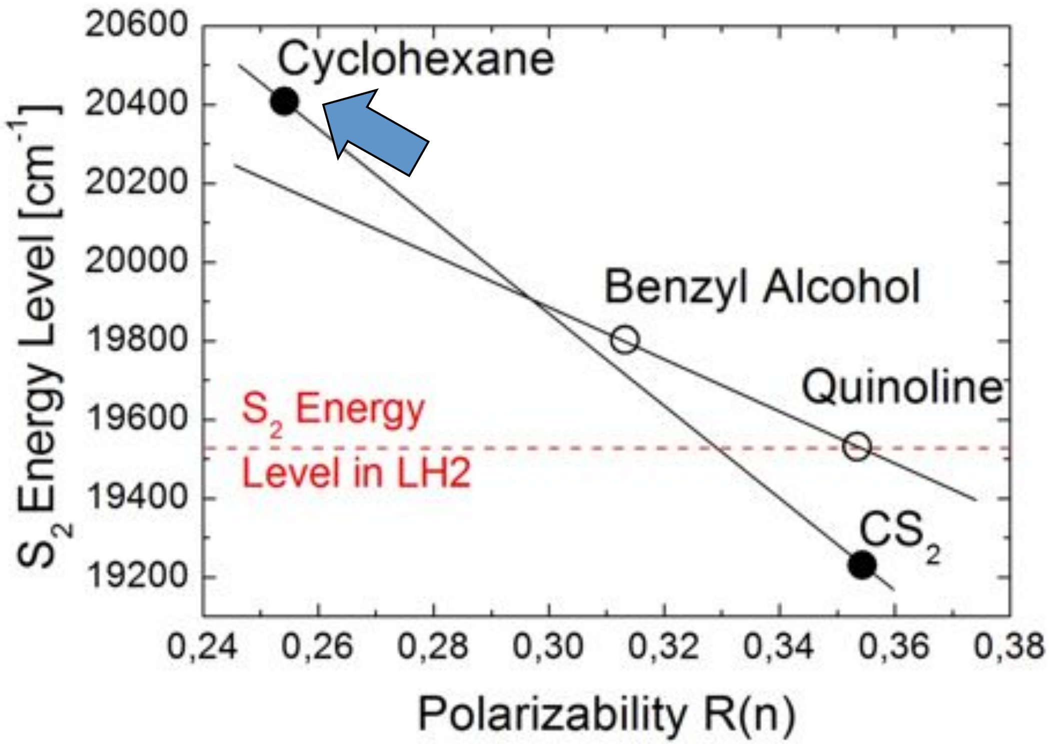




Experimental Results (II)

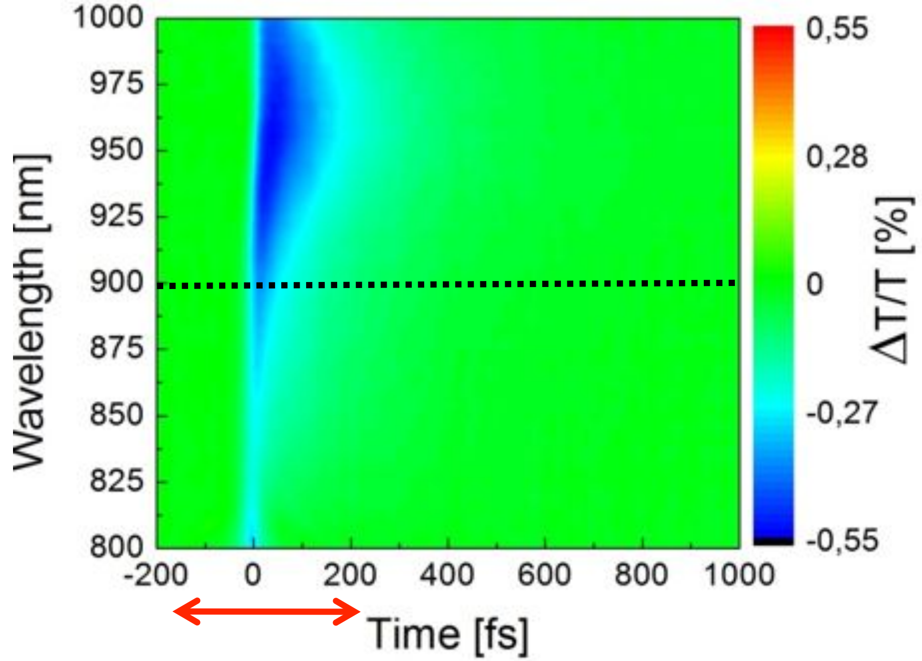
1. Spheroidene in CS_2

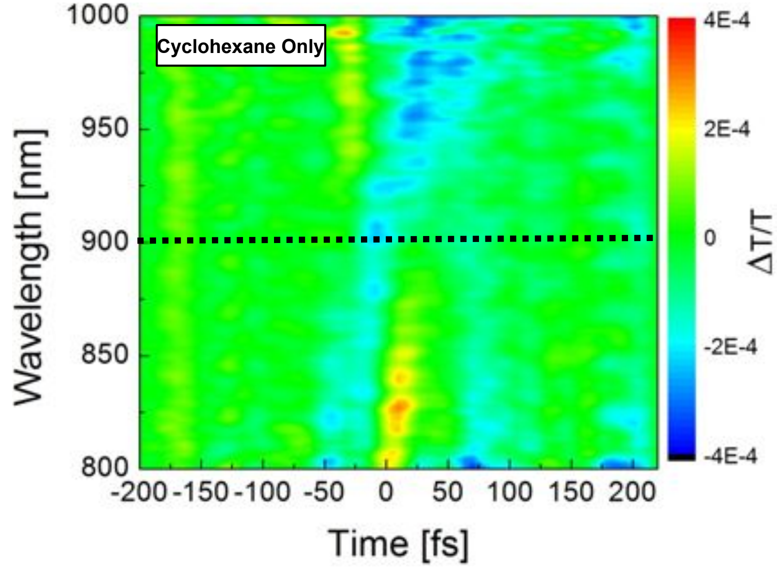
2. Spheroidene in Cyclohexane

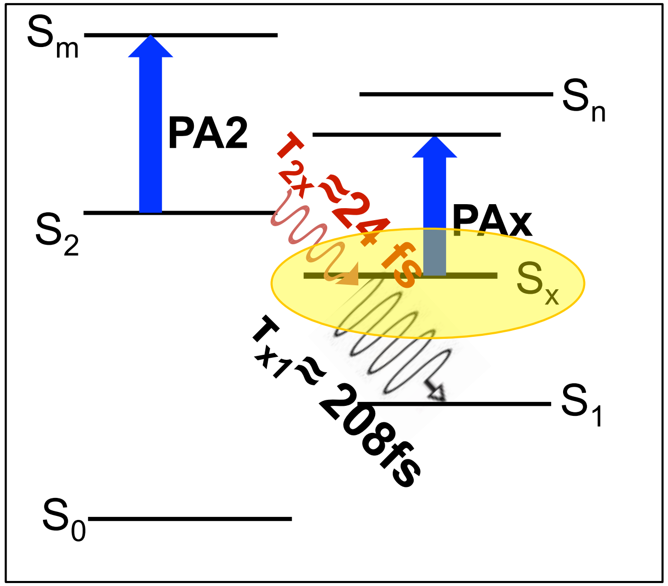


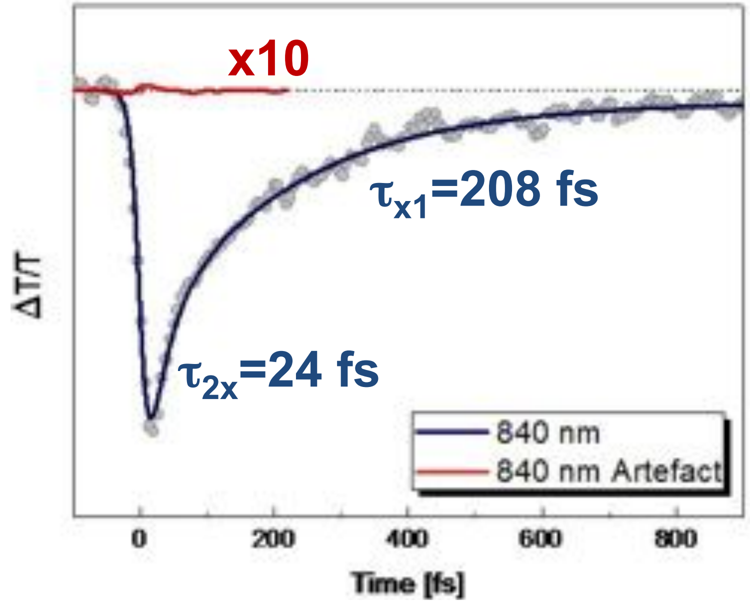
M. Maiuri, D. Polli, D. Brida, L. Lüer, A. M. LaFountain, M. Fuciman, R. J. Cogdell, H. A. Frank, and G. Cerullo, *Phys. Chem. Chem. Phys*. **14**, 6312-6319 (2012).

Intermediate State in Cyclohexane









Efficiencies

Commercial single-junction silicon cell η≈18%.

Modern commercial electrolyzers η≈80%

⇒ PV water splitting **η≈14%**.

Quantum efficiency (percentage of absorbed photons that give rise to stable photoproducts) **η≈100%.**

Energy conversion efficiency (ECE, usable electrical or harvestable chemical energy output divided by the total incident solar energy) **η≈1%**.

Energy conversion efficiency (ECE)

Table I: Annual Biofuel Production and Energy Conversion Efficiency by Photosynthetic Organisms and Electrical Energy Production by a Photovoltaic Cell.			
Oil Producer	Fuel Production [kg/(ha year)]	Energetic Equivalent [kWh/(ha year)]	ECE (%)
Oil palm	3,600–4,000	33,900–37,700	0.16–0.18
Jatropha	2,100–2,800	19,800–26,400	0.09–0.13
Tung oil tree (China)	1,800–2,700	17,000–25,500	0.08–0.12
Sugarcane	2,450	16,000	0.08
Castor oil plant	1,200–2,000	11,300–18,900	0.05–0.09
Cassava	1,020	6,600	0.03
Microalgae	91,000	956,000	4.6
Si-based PV cell		3×10^6	14.3

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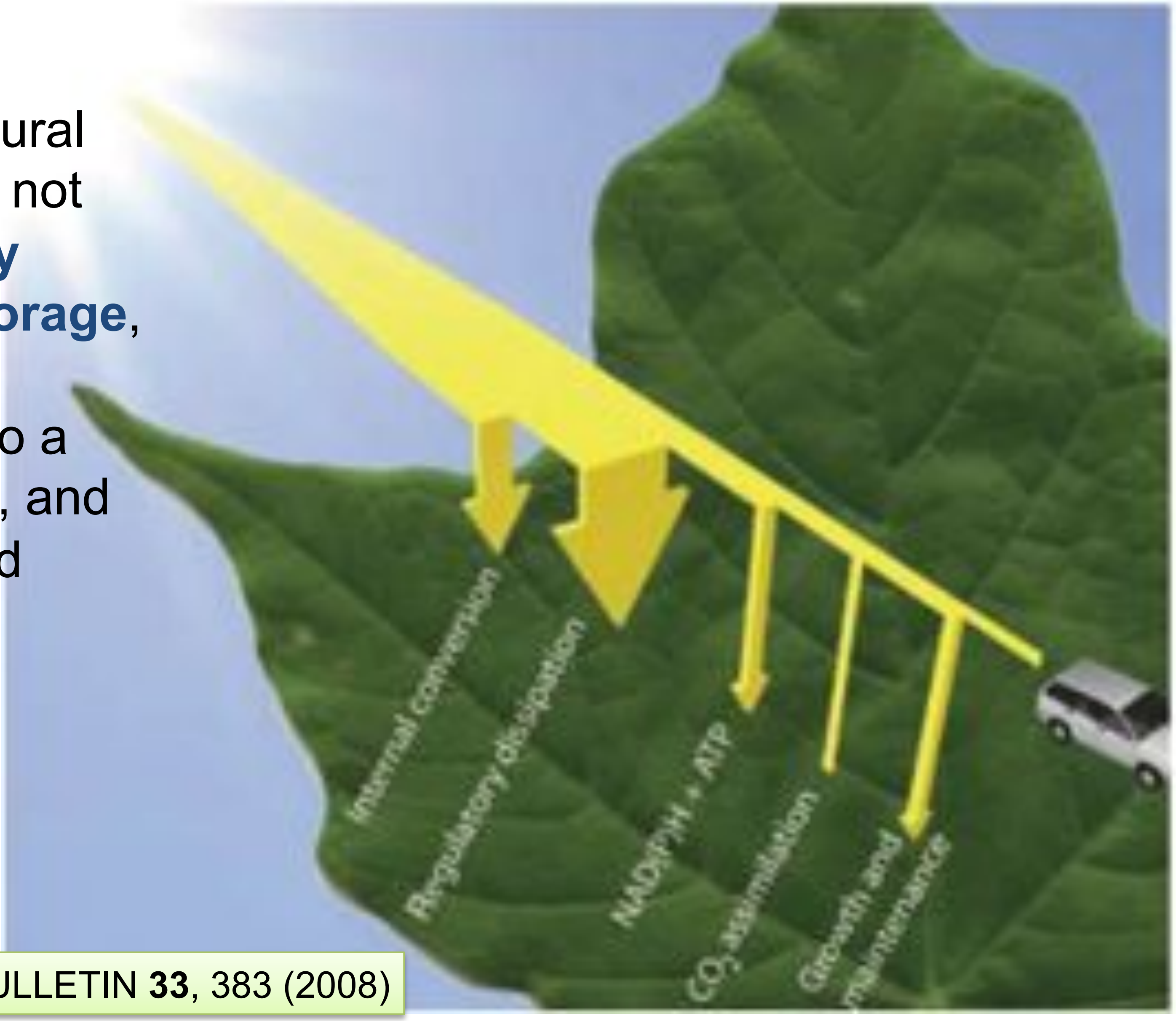
Photosynthesis = “add-on module”

The evolution of natural photosynthesis was not driven by **maximally efficient energy storage**, but rather allowed organisms to tap into a **new power source**, and thus to **colonize** and **survive** in new environments.



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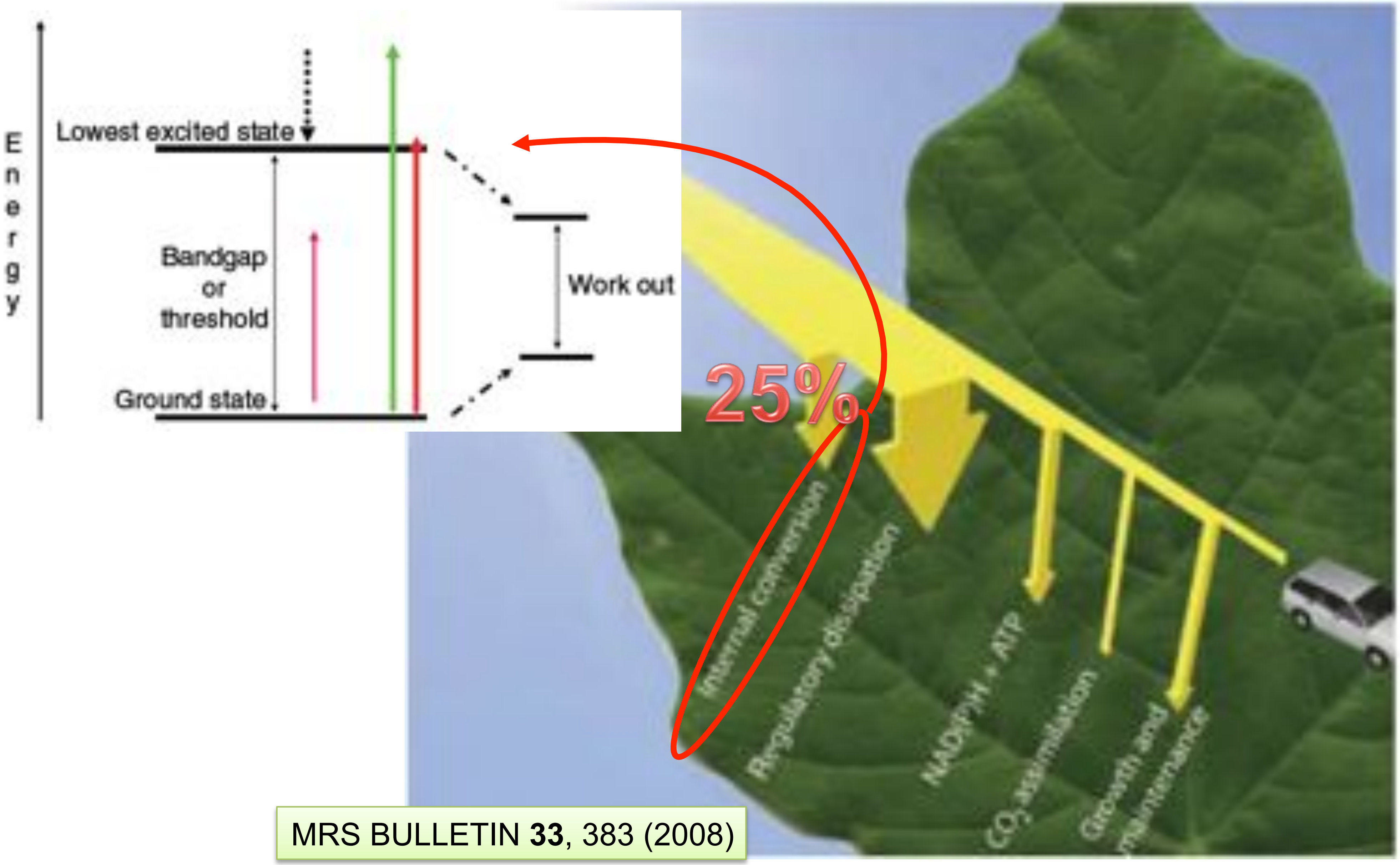
Internal conversion



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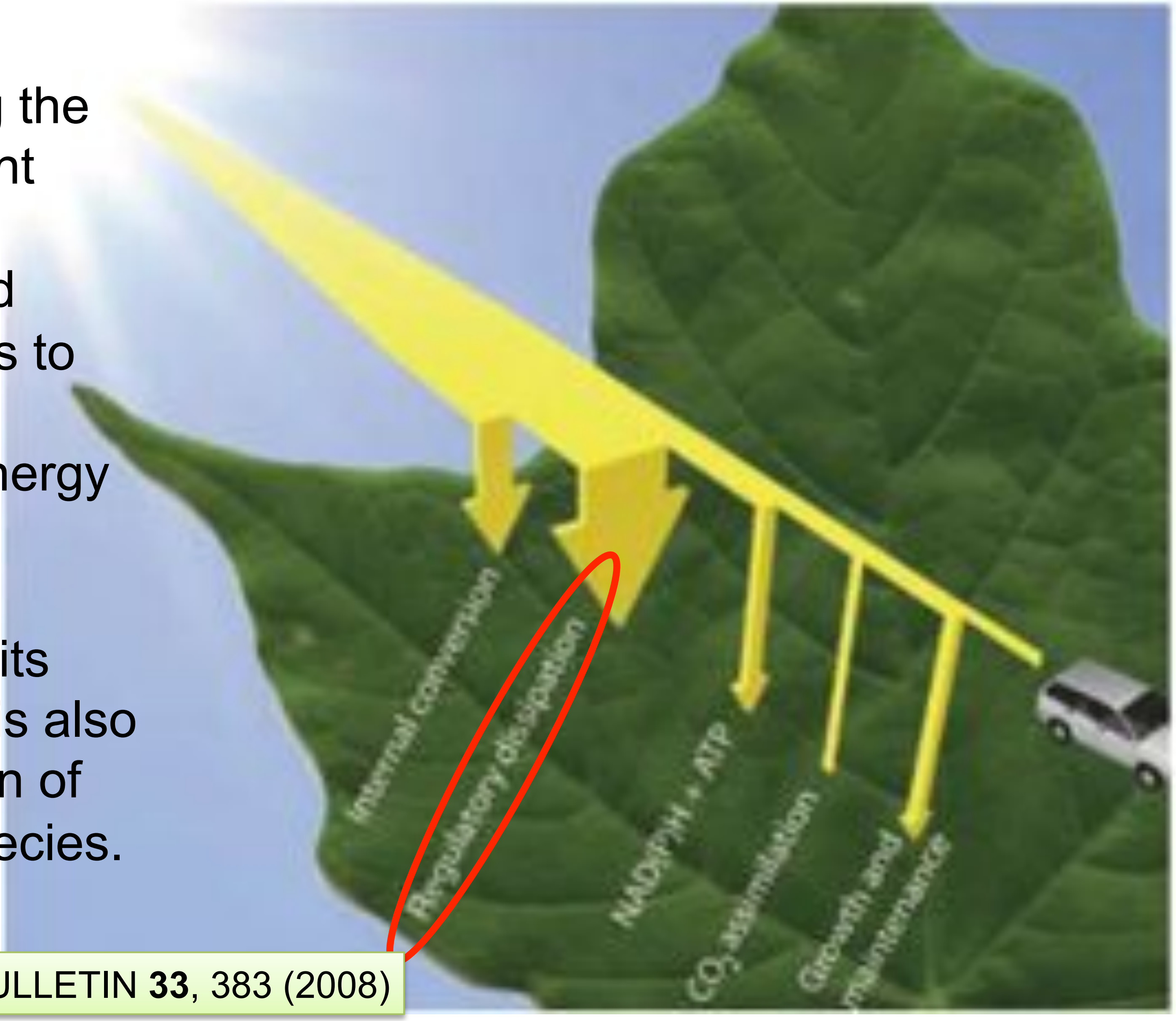
Regulatory dissipation

Rather than solving the problem of inefficient carbon fixation, plants have evolved control mechanisms to dissipate as heat much of the light energy they absorb under conditions where CO2 availability limits photosynthesis. This also avoids the formation of reactive oxygen species.



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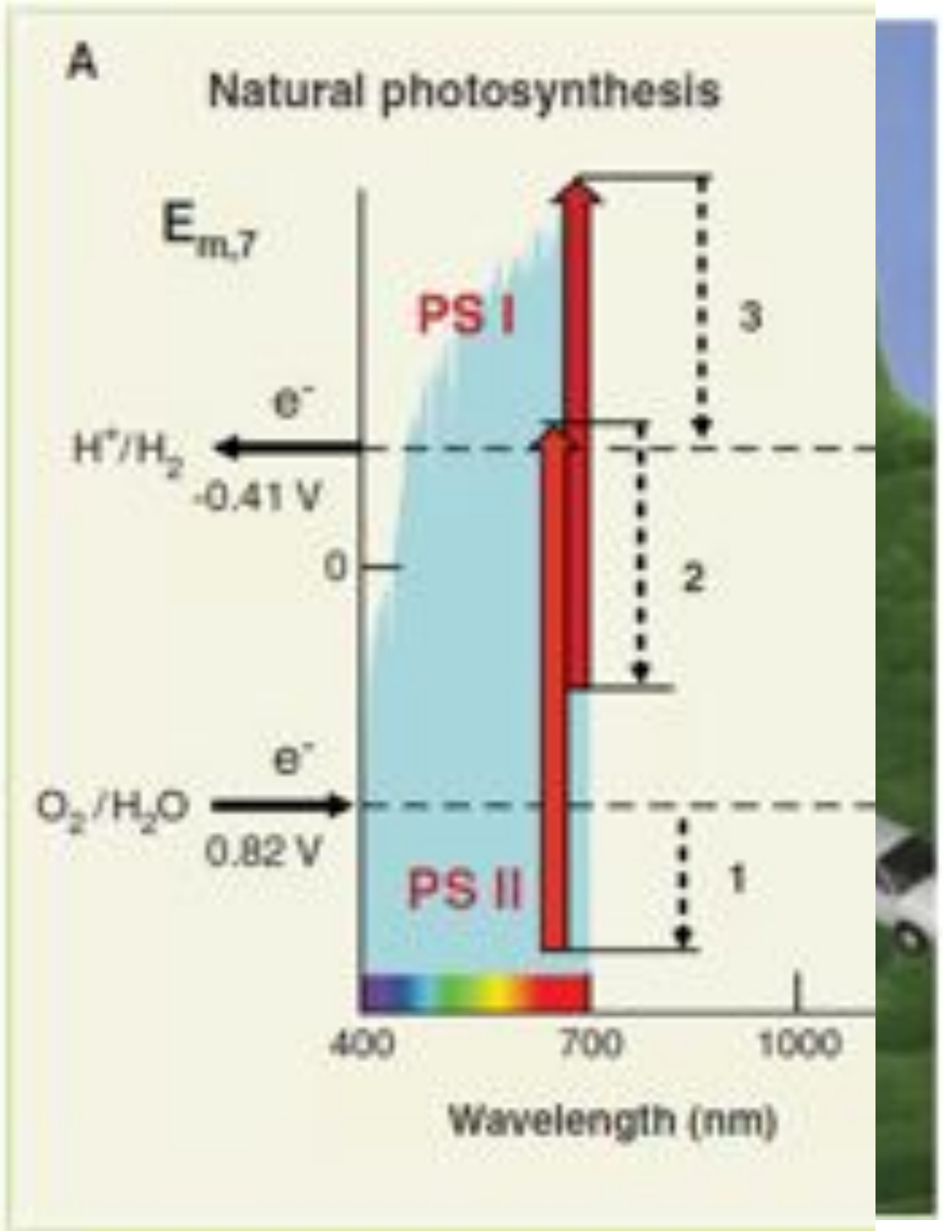
Legacy bioenergetics

“Without a large increase in energy conversion efficiency, land-grown biofuel production and food production will ***compete for land****, a largely untenable compromise given the c… al status of the world’s*



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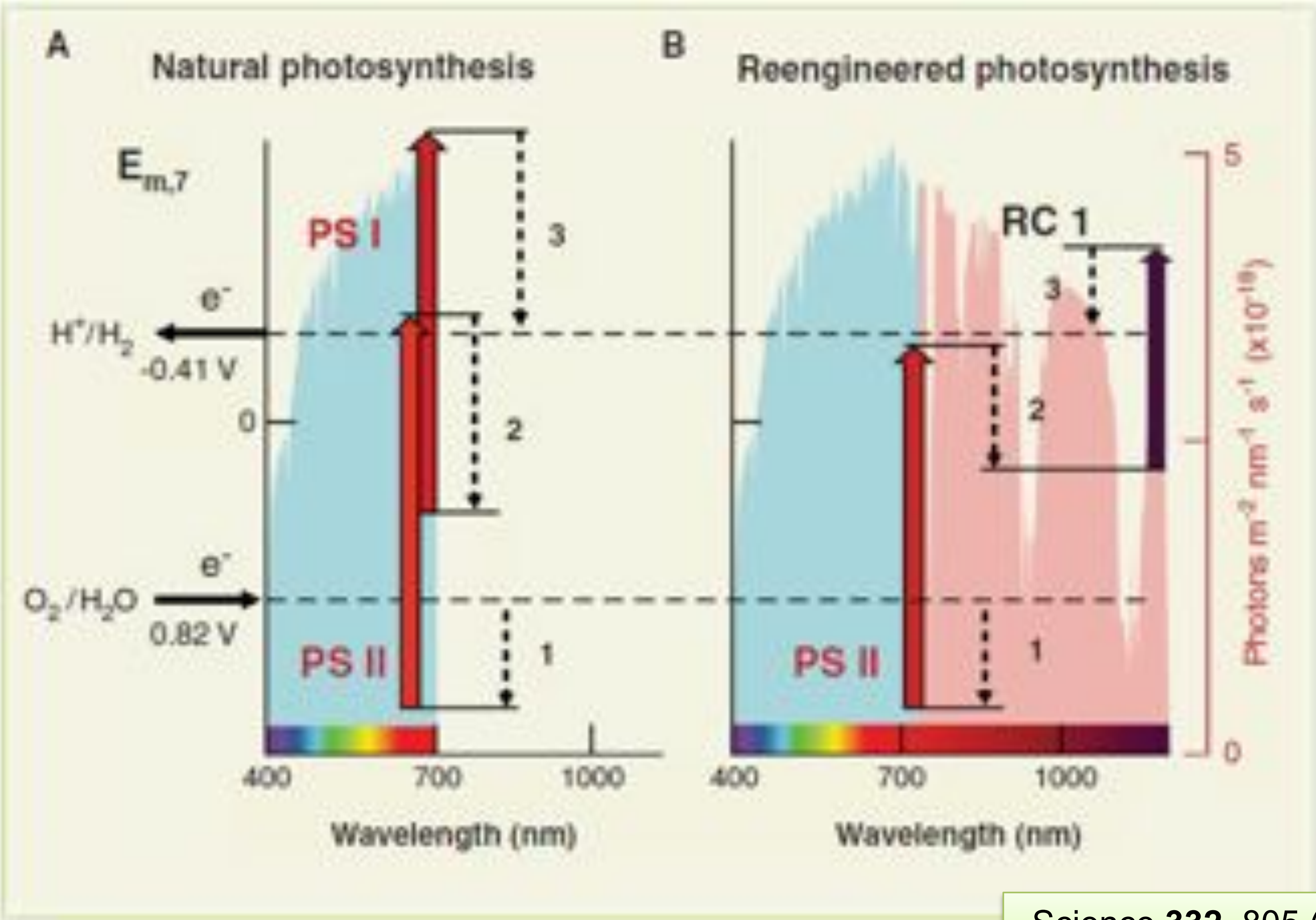
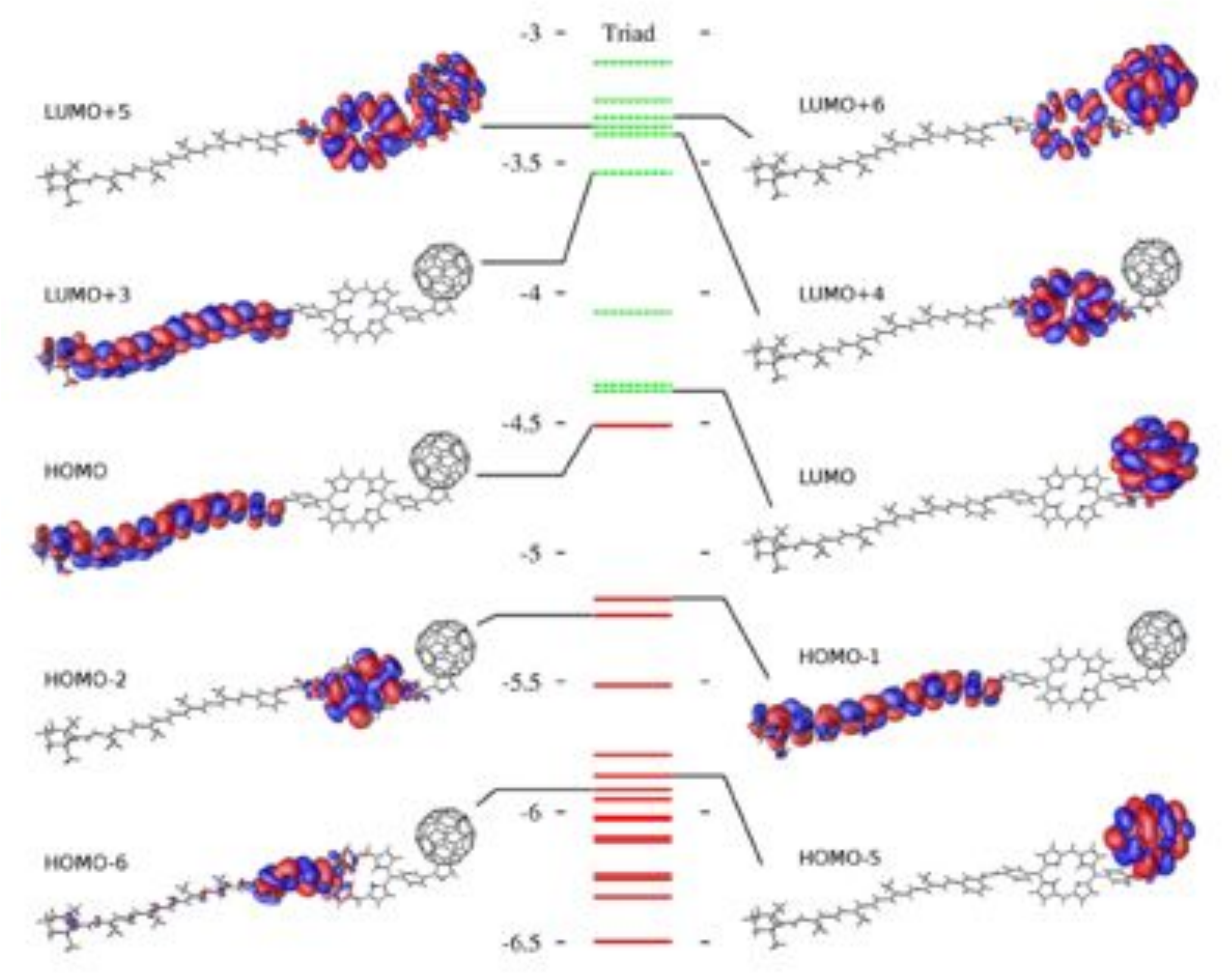
Re-engineered photosynthesis



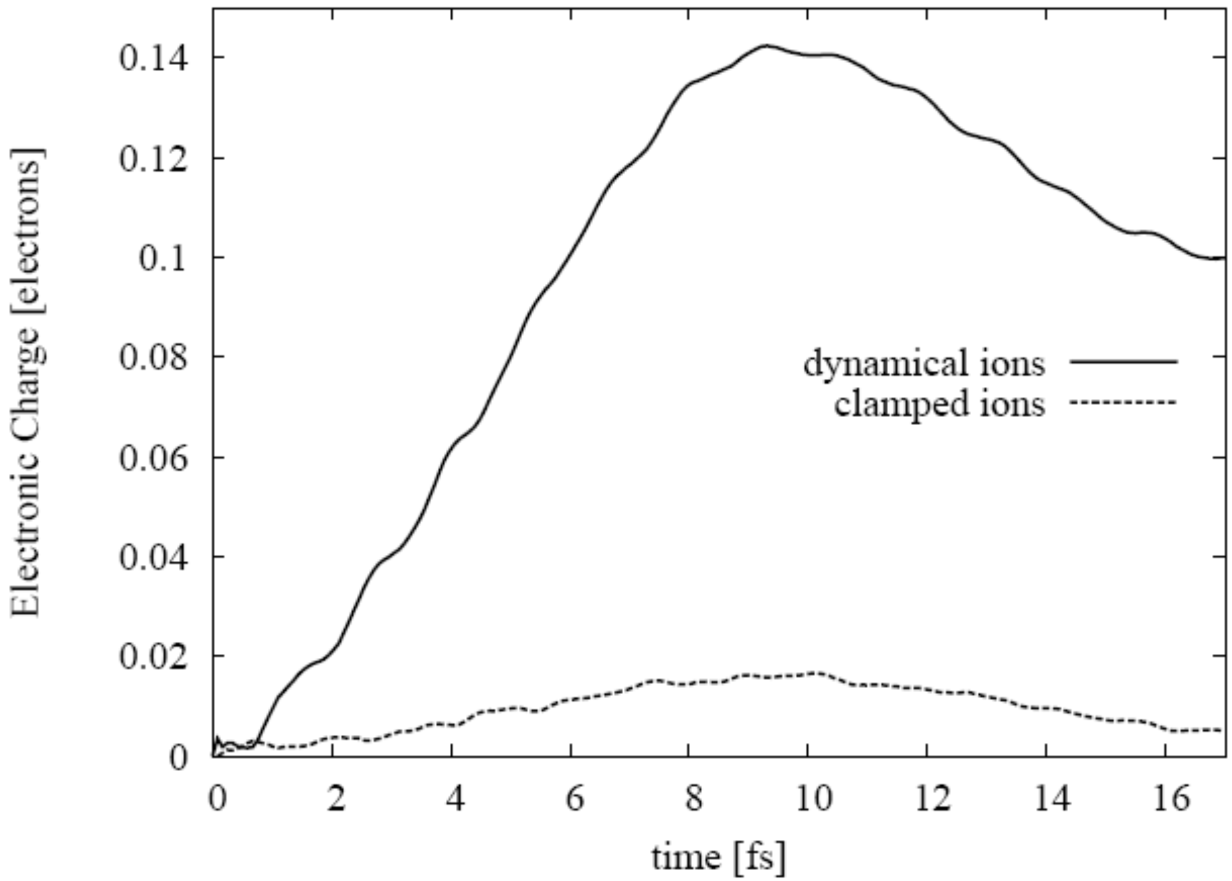
Science **332**, 805 (2011)

Triad electronic structure



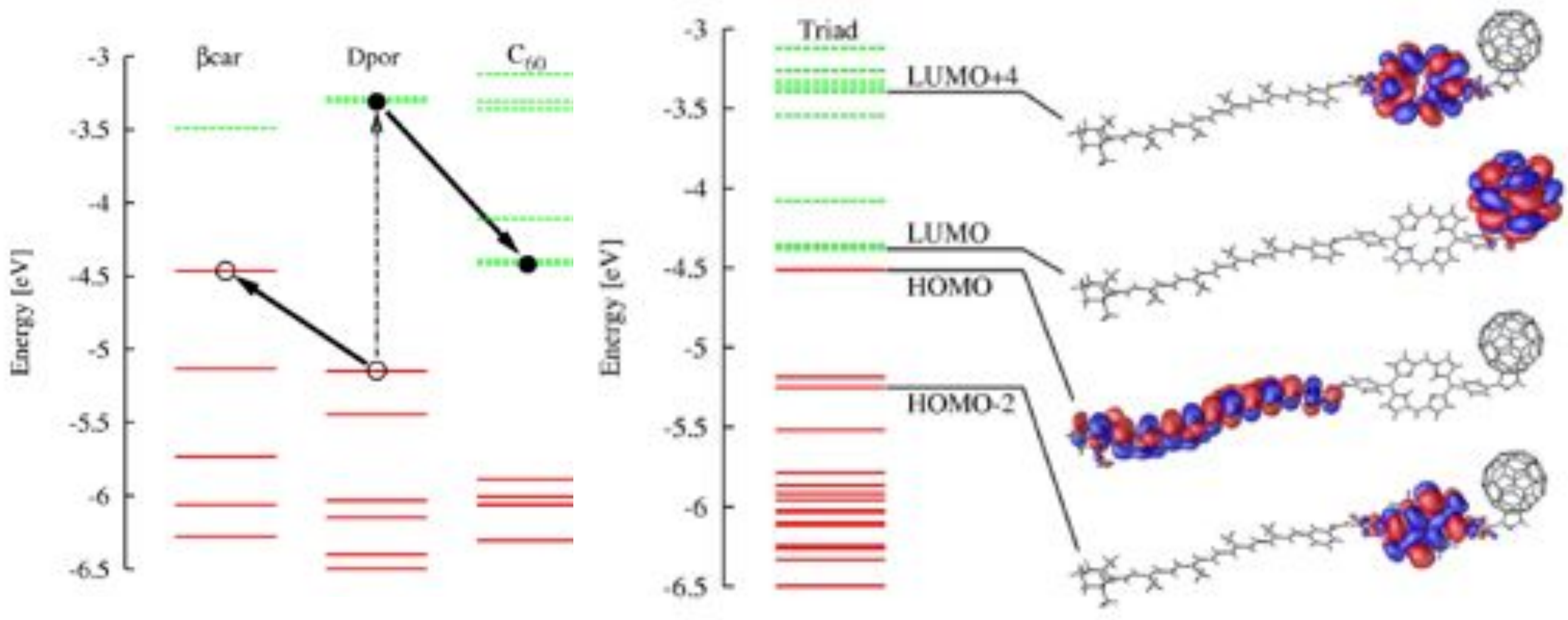
Courtesy: Nicola Spallanzani, Franca Manghi and Elisa Molinari (U Modena)

Triad: photoinduced charge transfer dynamics



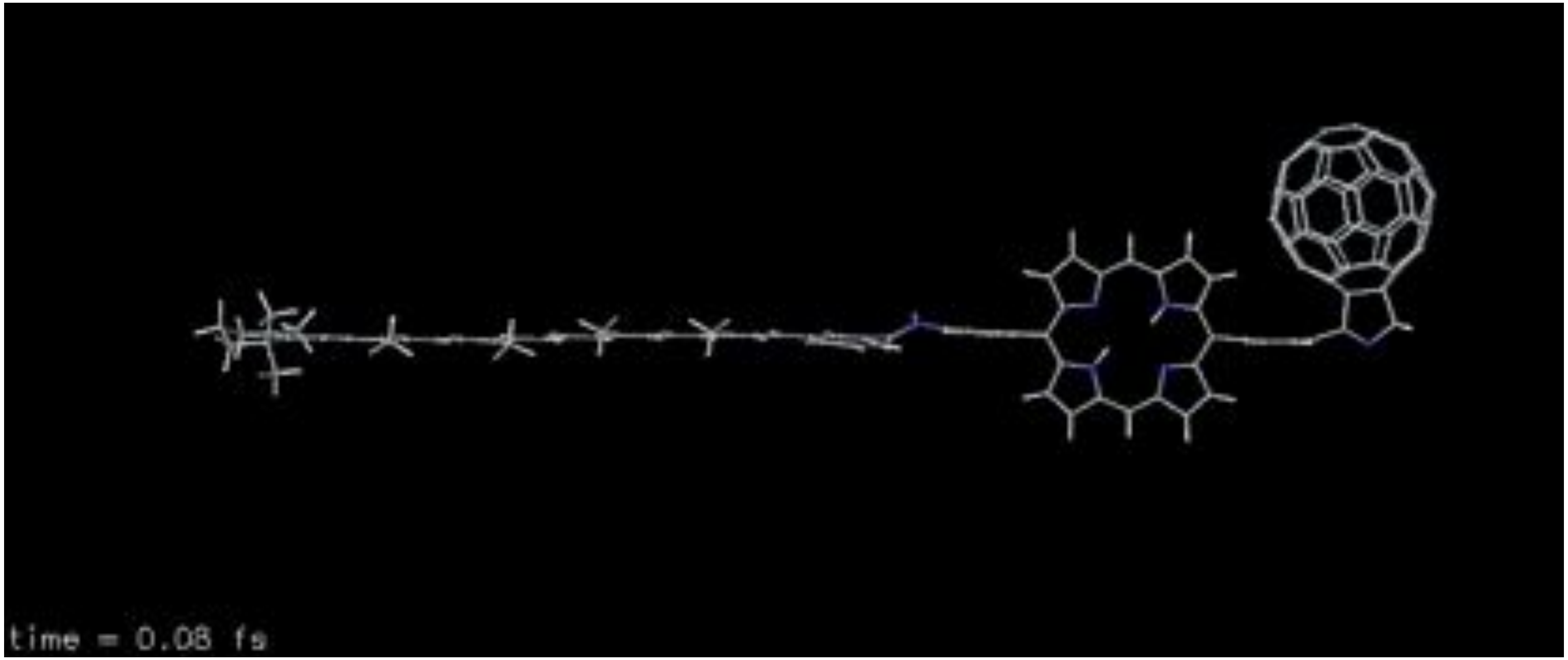
Courtesy: Nicola Spallanzani, Franca Manghi and Elisa Molinari (U Modena)

Triad: photoinduced charge separation scheme



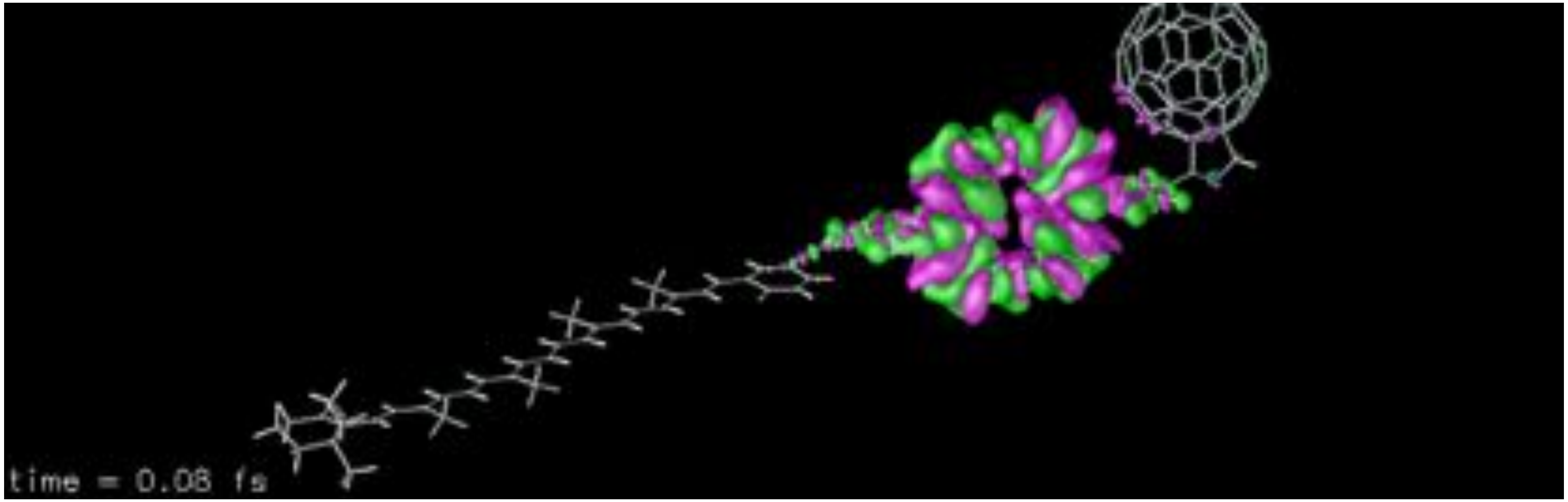
Courtesy: Nicola Spallanzani, Franca Manghi and Elisa Molinari (U Modena)

Coherent dynamics – DFT Simulations



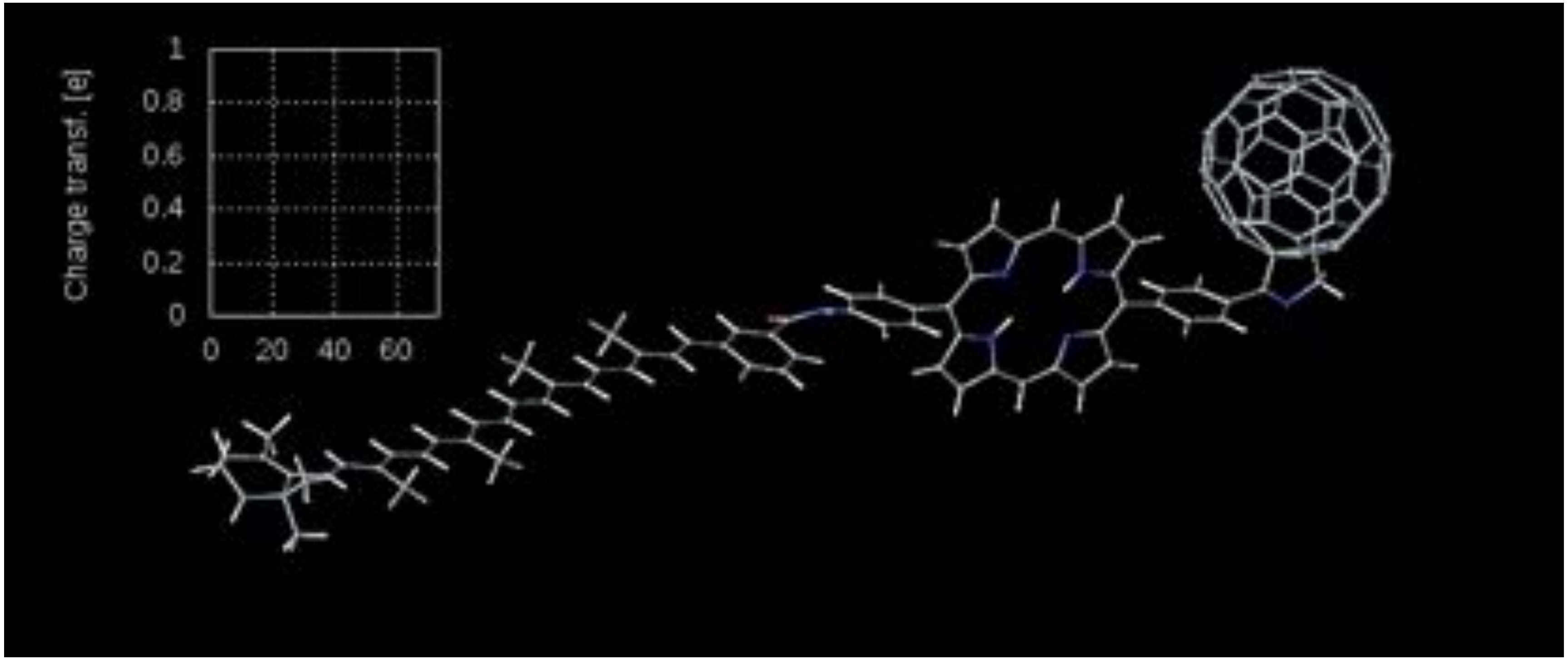
C. A. Rozzi, S. M. Falke et al., Nature Comm 4, 1602 (2013).

Coherent dynamics – DFT Simulations



Linker groups locked

Coherent dynamics – DFT Simulations



Motion of the ionic lattice