Variations of pump-probe spectroscopy

Bacteriorhodopsin, summary of:

- Widely investigated:
  - Nature – 34 papers (1990 – 2012)
  - Science – 43 papers(1990 – 2012)
  - PNAS -173 papers (1990 – 2012)

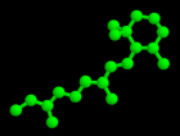
(Source: Web of science)

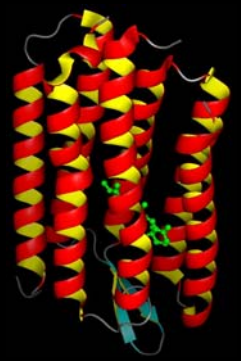
Function:

- Light drive proton pump that pushes protons across the membrane against the direction of the electric field.
- Found in purple membranes of *Halobacterium salinarium, up to 90% of membrane mass.*

Structure: membrane protein

- Structure resolved to 1.65 Å.
- 7 alpha helices containing a retinal chromophore





Advantages:

- Chemically stable and photostable
- Well known structure, easy to crystalize
- Bacteria grow a lot of it
- Fast, photoactive and therefore interesting
- Can be used as biomolecular tool or a model system for photoreactions

Isomerization of Retinal

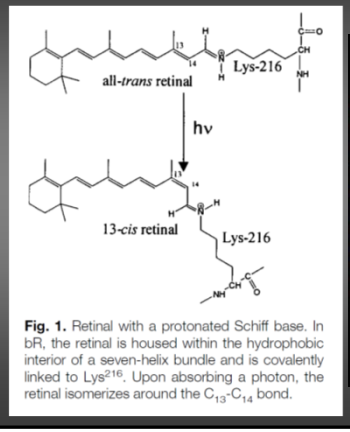
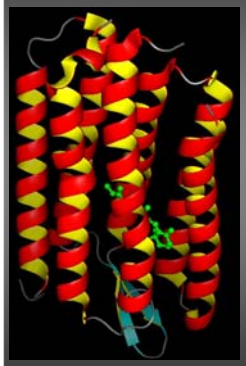
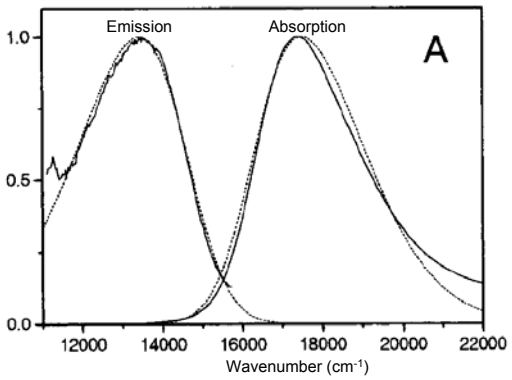


Fig. 1. Retinal with a protonated Schiff base. In bR, the retinal is housed within the hydrophobic interior of a seven-helix bundle and is covalently linked to Lys^{216}. Upon absorbing a photon, the retinal isomerizes around the C_{13}-C_{14} bond.



Absorption and emission



Observation:

- ***The decays can be well fitted as a sum of three exponential decay components with time constants in the range of 90 fs-240 fs, 0.6 ps-0.9 ps, and 9.0–13.0 ps.***
- **Fluorescence disappears on sub-ps time scale!**

Du et al. Biophysical chemistry, 1993

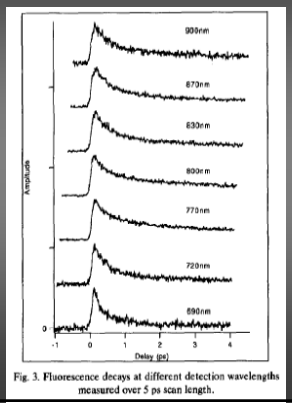
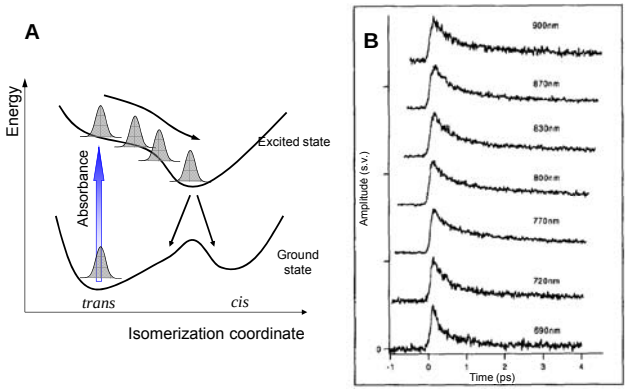


Fig. 3. Fluorescence decays at different detection wavelengths measured over 5 ps scan length.



M. Du and G.R. Fleming, *Biophysical Chemistry*, 1993. **48**(2): p. 101-111.

Pump-probe

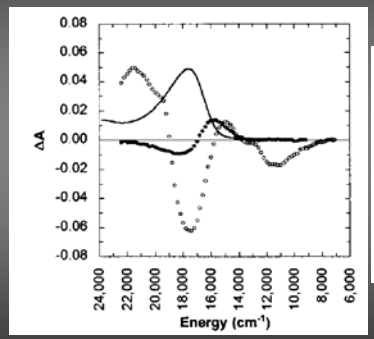
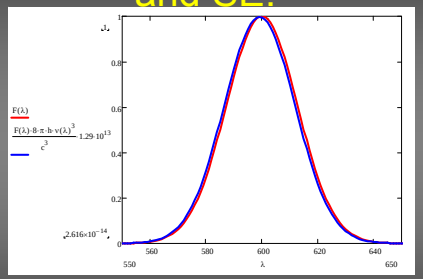


Fig. 3. Time-resolved absorbance spectra of bR recorded (*50*) at 0.316 ps (open circles) and 31.6 ps (filled circles). In the 0.316-ps spectrum, the negative-going feature centered at 17,600 cm^{-1} corresponds to photon-induced depletion of the ground-state absorbance; the negative-going feature peaked near 11,000 cm^{-1} corresponds to stimulated emission. Positive-going features correspond to excited-state or photoproduct absorbances. The 31.6-ps spectrum consists only of depleted ground-state and photoproduct absorbances. For comparison, a scaled equilibrium absorbance spectrum is shown (thick line). [Adapted from figure 2 of (*35*); copyright 1996, U.S. National Academy of Sciences]

Gai et al. Science 1998

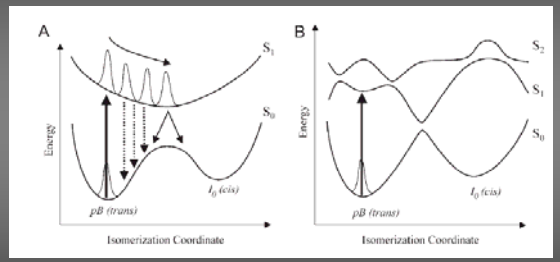
Relationship between fluorescence and SE:

$$A_{\hat{n}} = \frac{8\pi h\nu_{\hat{n}}^3}{c^3} B_{\hat{n}}$$



At optical frequencies the fluorescence and stimulated emission spectra should be nearly identical

Two models, which one do we believe?



Temperature dependence: from 0.5 ps (RT) to 60 ps (77K)
Fluorescence and SE spectra: Einstein says

$$A_{\hat{n}} = \frac{8\pi h\nu_{\hat{n}}^3}{c^3} B_{\hat{n}}$$

No detailed information about the structural changes of the molecule

....solution: go infrared! ☺

The probe beam needs to be in the mid-IR

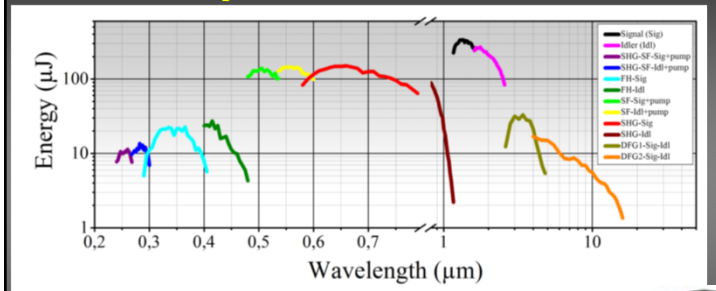
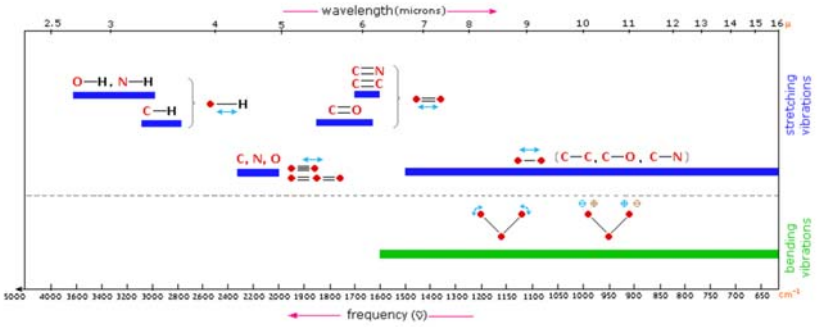


Fig. 11. Tuning curves of TOPAS-prime with VIS and IR extensions when pumped by the 55 fs, 1.75 mJ, 100 kHz burst-mode pulses from the PP-laser.

Molecular vibration frequencies



Vibrational features of *cis* appear within < 1ps!

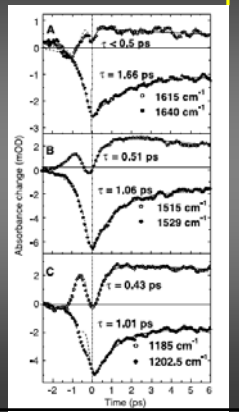
The IR spectrum of *cis* known from FTIR measurements forms in <1 ps.

First evidence that it is isomerization that causes fluorescence to disappear so fast.

C—NH

C=C

C—C



Herbst et al. Science, 2002

Comparison of vibrational features in the spectrum

Top: Visible pump – mid IR probe;
Bottom: Step-scan FTIR (15 ns)

Herbst et al. Science, 2002

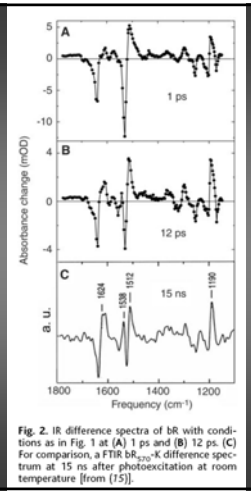


Fig. 2. IR difference spectra of bR with conditions as in Fig. 1 at (A) 1 ps and (B) 12 ps. (C) For comparison, a FTIR bR_{570}–K difference spectrum at 15 ns after photoexcitation at room temperature [from (15)].

What is the function of the protein?...

....Solution: go UV! ☺

Protein role in BR isomerization?...

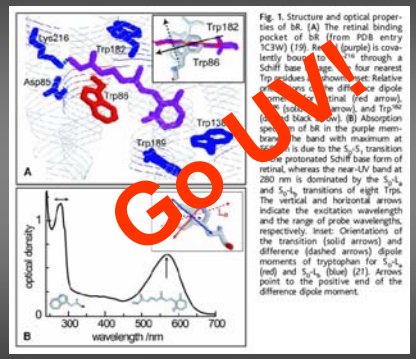
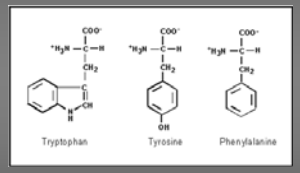


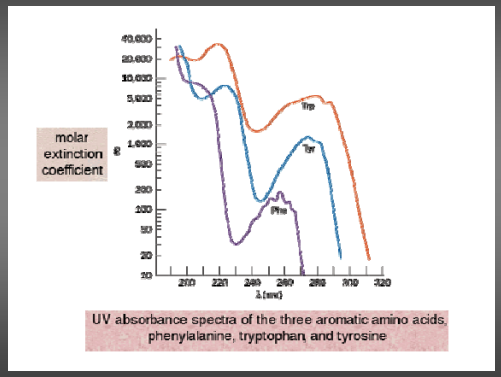
Fig. 1. Structure and optical properties of bR. (A) The retinal binding pocket of bR (from PDB entry 1C3W) (19). Retinal (purple) is covalently bound to Lys216 through a Schiff base linkage. The four nearest Trp residues are shown in cyan. Relative orientations of the difference dipole moments of all-trans retinal (red arrow), 13-cis (isotope arrow), and Trp^{182} (cyan and black arrow). (B) Absorption spectrum of bR in the purple membrane. The band with maximum at 570 nm is due to the S_0–S_1 transition of the protonated Schiff base form of retinal, whereas the near-UV band at 280 nm is dominated by the S_0–L_a and S_0–L_b transitions of eight Trps. The vertical and horizontal arrows indicate the excitation wavelength and the range of probe wavelengths, respectively. Inset: Orientations of the transition (solid arrows) and difference (dashed arrows) dipole moments of tryptophan for S_0–L_a (red) and S_0–L_b (blue) (21). Arrows point to the positive end of the difference dipole moment.

GO UV!

Schenkl et al. Science 2005

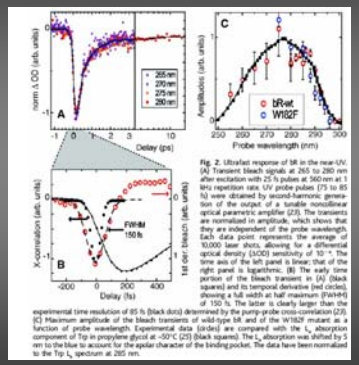
Protein role in BR isomerization?...





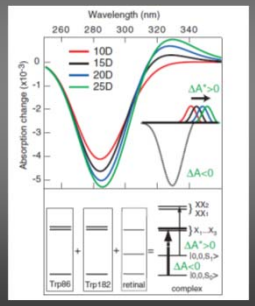
UV absorbance spectra of the three aromatic amino acids, phenylalanine, tryptophan, and tyrosine

Protein reacting to electric field of retinal



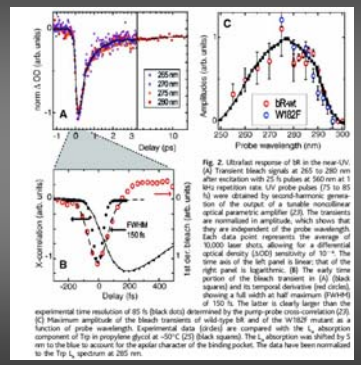
Schenkl et al. Science 2005

Tryptophan acts as an electric field probe inside the protein highlighting the electric field evolution after the excitation.



Complex: Retinal+2Trp's

Protein reacting to electric field of retinal



Schenkl et al. Science 2005

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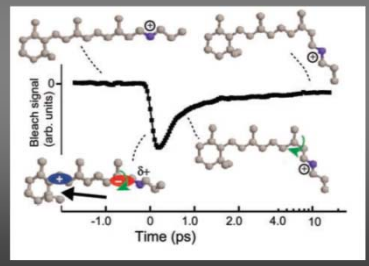


Adding a twist...

Advanced ultrafast spectroscopies

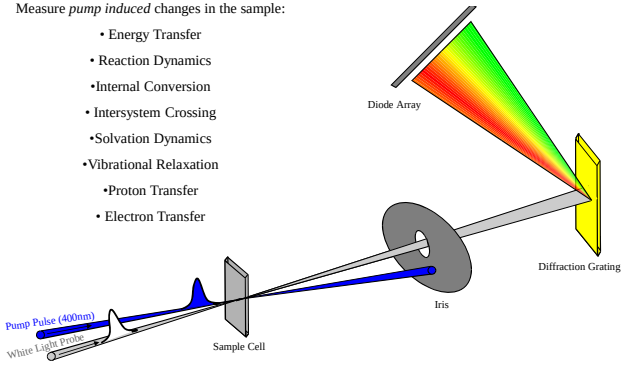
Twist #1:

Multi-pulse transient absorption

Dispersed Pump-Probe Experimental Setup

Measure *pump induced* changes in the sample:

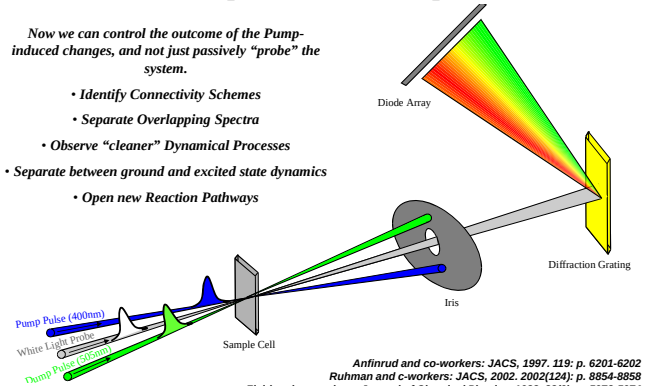
- Energy Transfer
- Reaction Dynamics
- Internal Conversion
- Intersystem Crossing
- Solvation Dynamics
- Vibrational Relaxation
- Proton Transfer
- Electron Transfer



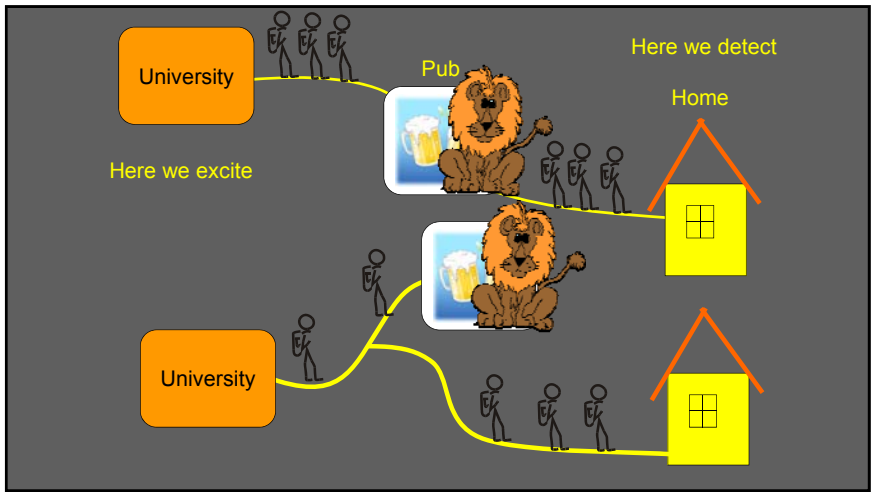
Dispersed Multi-Pulse Experimental Setup

Now we can control the outcome of the Pump-induced changes, and not just passively "probe" the system.

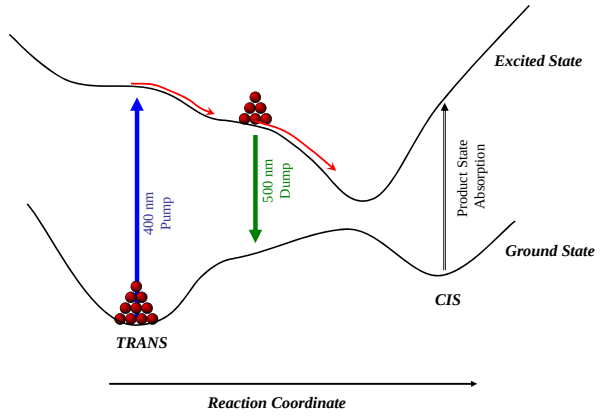
- ***Identify Connectivity Schemes***
- ***Separate Overlapping Spectra***
- ***Observe "cleaner" Dynamical Processes***
- ***Separate between ground and excited state dynamics***
- ***Open new Reaction Pathways***



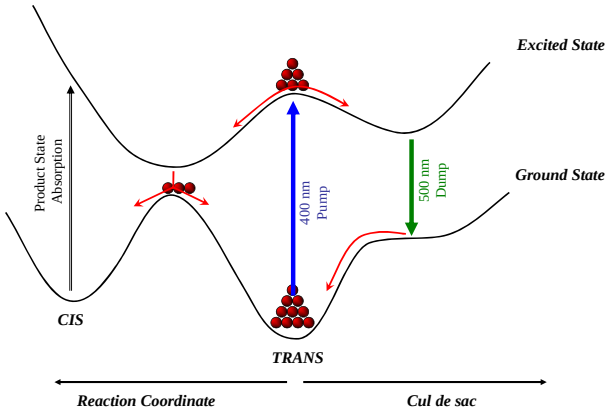
Anfinrud and co-workers: JACS, 1997. 119: p. 6201-6202
Ruhman and c-workers: JACS, 2002. 2002(124): p. 8854-8858
Field and co-workers: Journal of Chemical Physics, 1988. 88(9): p. 5972-5974



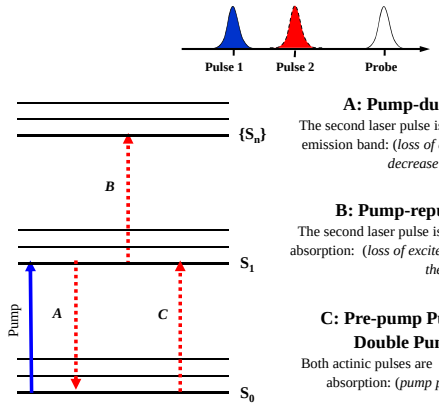
Sequential Isomerization Dynamics



Branched Isomerization Dynamics



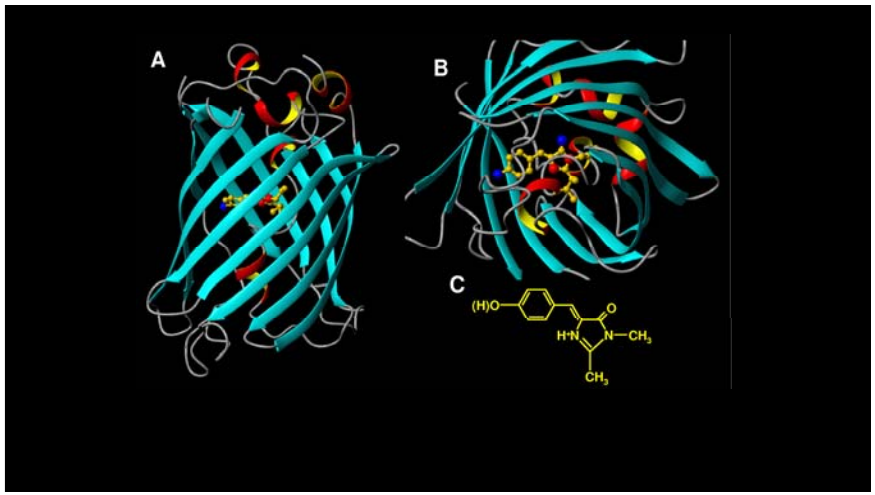
Multi-pulse Transient Absorption Spectroscopies



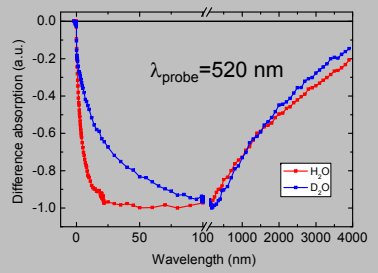
A: Pump-dump-probe (PDP)
The second laser pulse is resonant with the stimulated emission band: (*loss of excited population leading to decrease of all signals*)

B: Pump-repump-probe (PrPP)
The second laser pulse is resonant with an excited state absorption: (*loss of excited state signals with no effect on the bleach*)

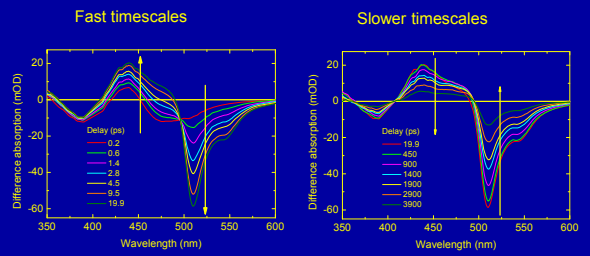
C: Pre-pump Pump-Probe (4P) and Double Pump-Probe (PPP)
Both actinic pulses are resonant with the ground state absorption: (*pump probe on the excited state*)



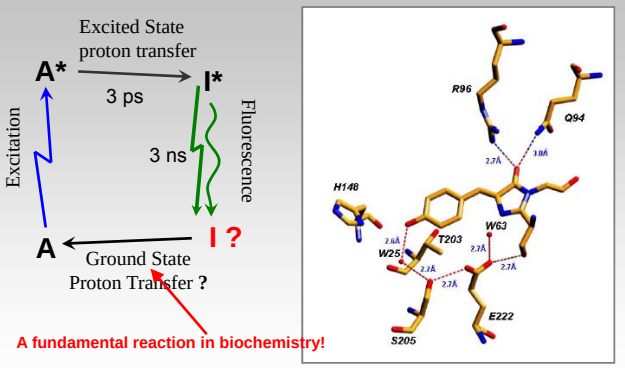
Kinetic Isotope Effect: evidence for proton transfer



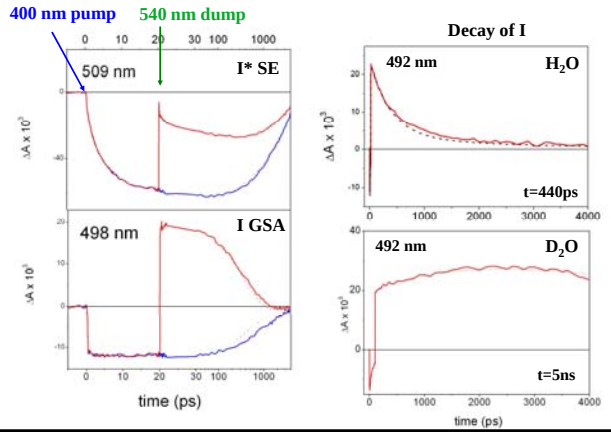
Excited state proton transfer in GFP



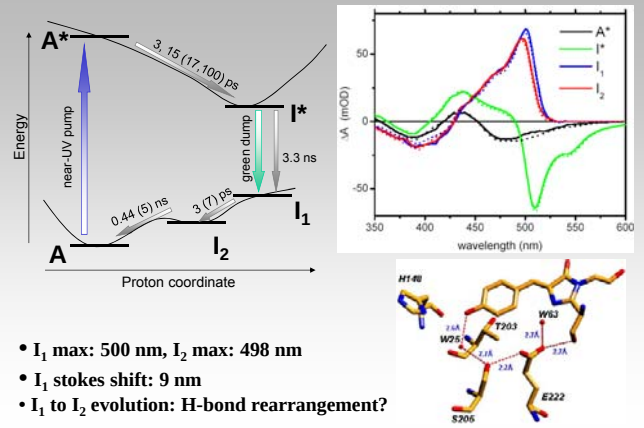
Idea: try to dump the excited state!



Pump-dump-probe spectroscopy on GFP



Spectra and lifetimes of Hidden Intermediates

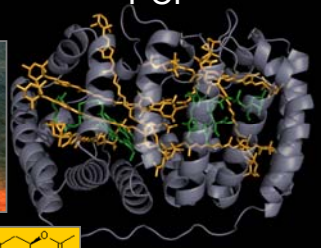


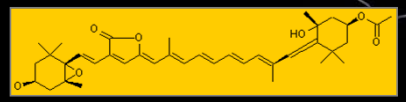
- **I_1 max: 500 nm, I_2 max: 498 nm**
- **I_1 stokes shift: 9 nm**
- **I_1 to I_2 evolution: H-bond rearrangement?**

Energy transfer in PCP: role of ICT state

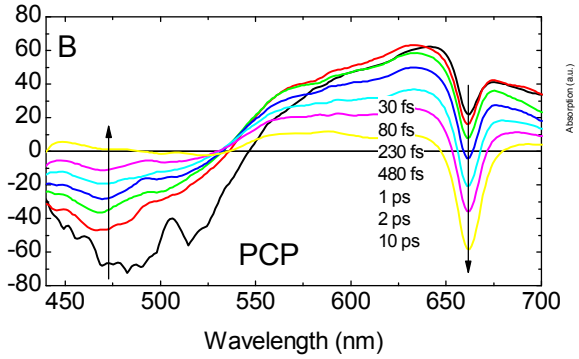
Red algae

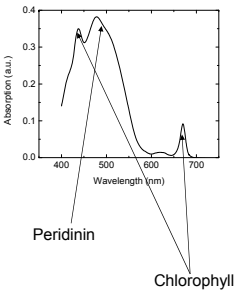
PCP





PCP harvesting light





For warm up: peridinin in solution

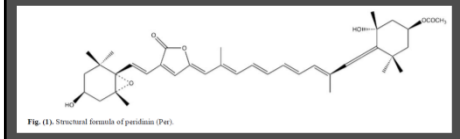


Fig. (1). Structural formula of peridinin (Per).

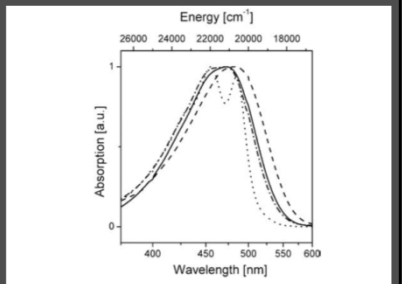
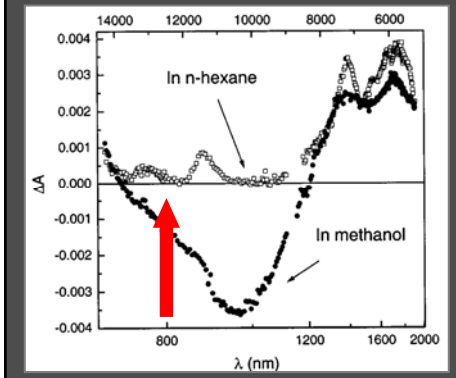


Fig. (2). Absorption spectra of Per in n-hexane (•••), acetonitrile (– • –), methanol ( ), and ethylene glycol (– – –). All spectra are normalized. Reprinted with permission from Zigmantas, D. ; Hiller, R.G. ; Yarsev, A. ; Sundstrom, V. ; Polivka, T. J. Phys. Chem. B 2003, 107, 5339-5348 Copyright 2003 American Chemical Society.

Near-IR transient Absorption spectra of peridinin



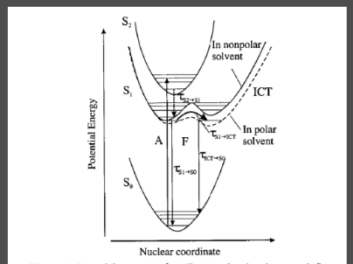
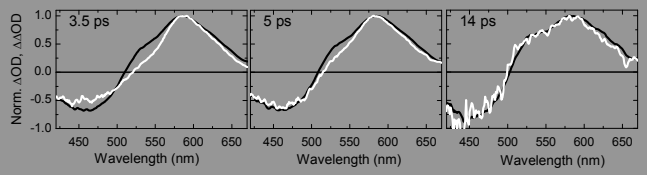


Figure 9. Potential energy surface diagram showing the ground, first, and second singlet excited states of peridinin in nonpolar and polar solvent environment. The S_1 state is strongly coupled with the ICT state. In nonpolar solvents, the barrier between the S_1 and ICT states is high and therefore the ICT state is not populated. In polar solvents, i.e., methanol, the polarity-affected barrier is diminished as the ICT state shifts to lower energy, therefore becoming populated. The transitions and corresponding time constants are shown for the peridinin in polar solvent.

Zigmantas *et al.*, *JPC A* **105, 2001**

Peridinin pump-dump-probe spectra

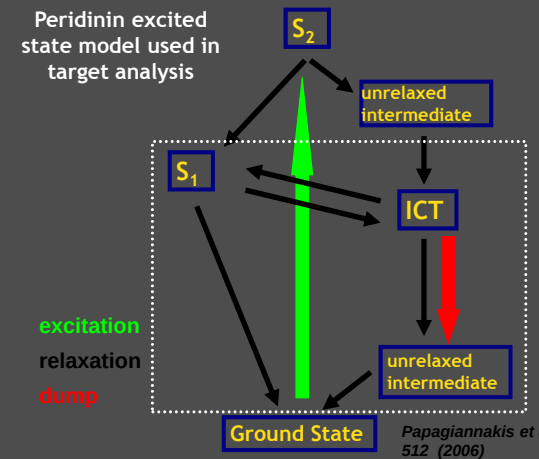
530-nm excitation, 800-nm dump at 3 ps



"normal" pump-probe ΔOD spectrum

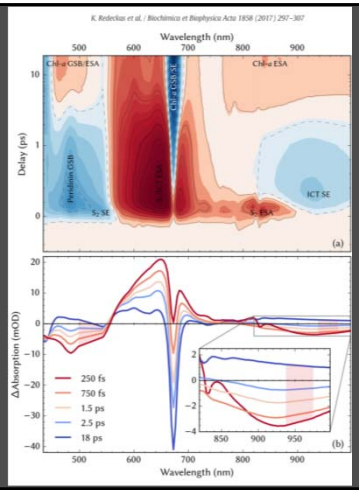
dump-induced difference spectrum

Peridinin excited state model used in target analysis

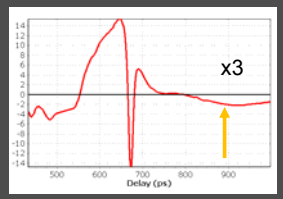


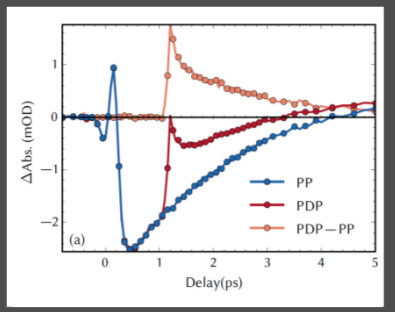
Papagiannakis et al., JPCB, 110, 512 (2006)

PCP Data: pump at 520 nm probe 440-1000 nm, dump 950 nm



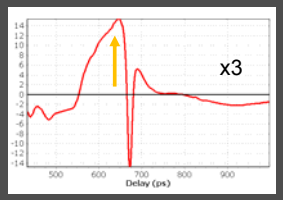
Dump effects at different wavelengths



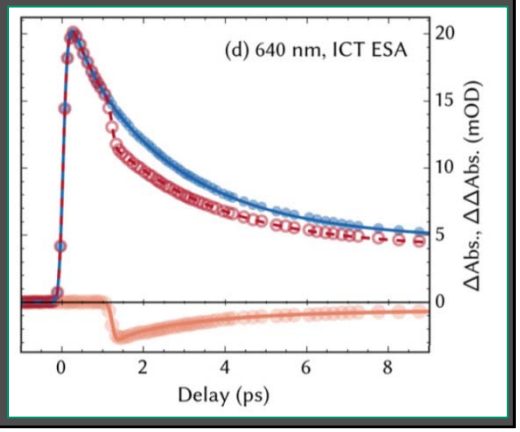


Almost 100% of signal is lost, then it recovers

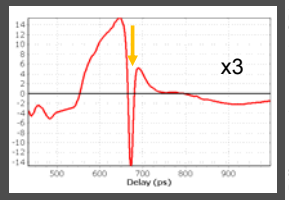
Dump effects at different wavelengths

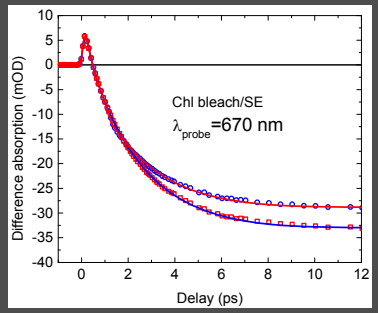


The loss is about 20% - overlapping signals?



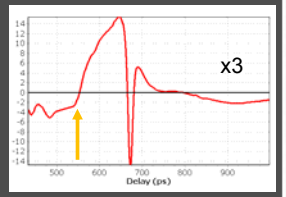
Dump effects at different wavelengths

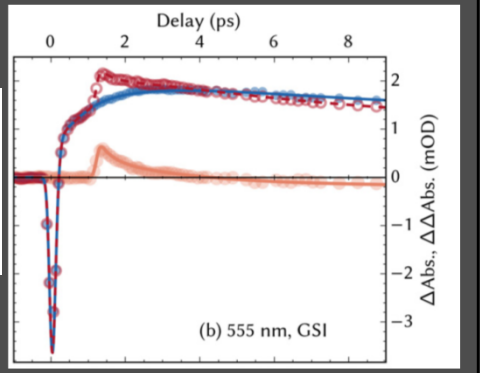




Initially, Chl a does not feel any influence of the dump.

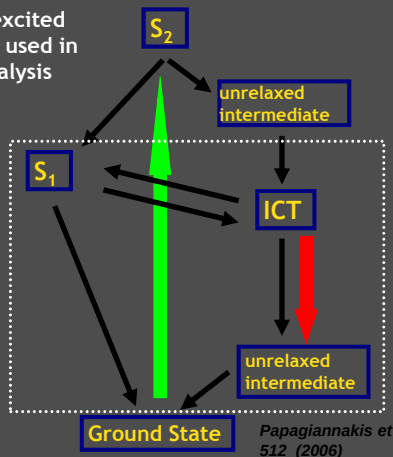
Dump effects at different wavelengths



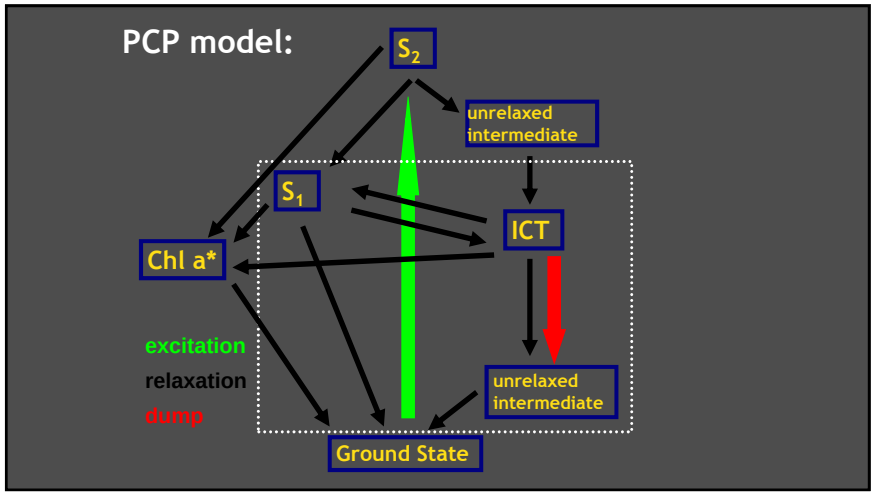


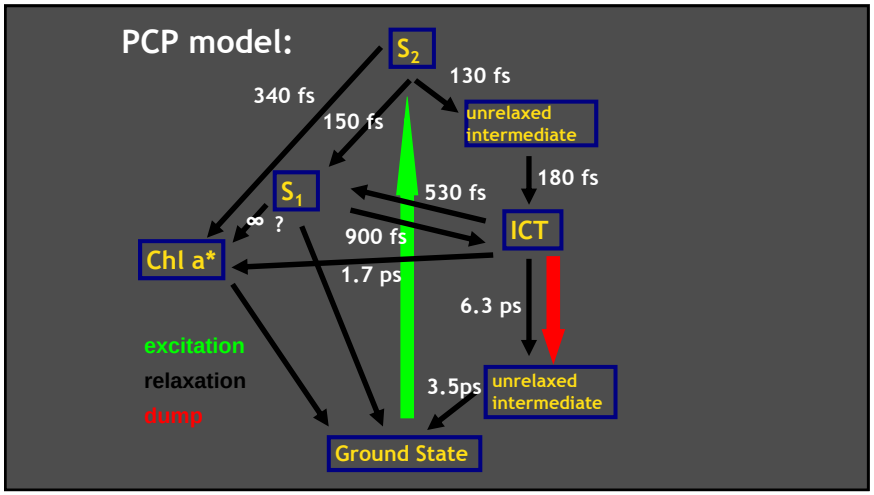
Dump produces *increase* in the IA signal – hot ground state?

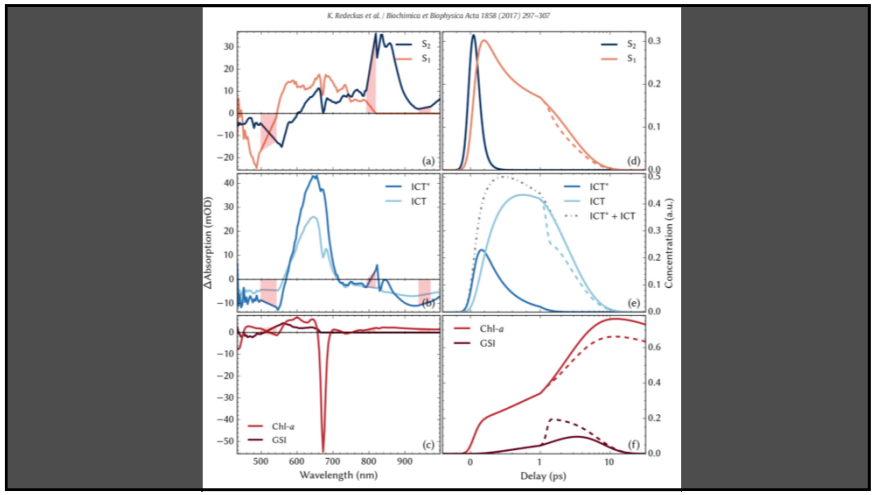
Peridinin excited state model used in target analysis



Papagiannakis et al., JPCB, 110, 512 (2006)

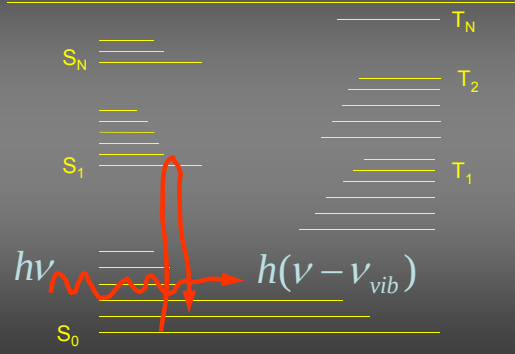






Twist #2: Femtosecond stimulated Raman spectroscopy (FSRS)

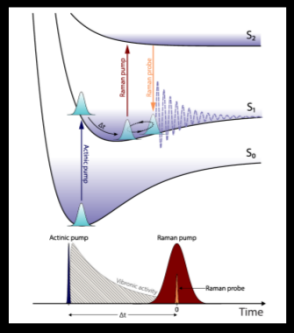
Raman scattering



Twist #2: Femtosecond stimulated Raman spectroscopy (FSRS)

- Playing around with electronic states is all good and well, however, the underlying structural changes are mostly guesswork.
- Raman spectroscopy is measuring vibrational frequencies, therefore it is directly sensitive to conformational changes in molecules.
- Raman spectroscopy is not prone to problems with midIR (bad detectors, ambient air absorption, etc.)
- However, to resolve narrow vibrational lines require narrow Raman Pump spectra (poor time resolution ~3 ps).
- Enter FSRS.

Twist #2: Femtosecond stimulated Raman spectroscopy (FSRS)

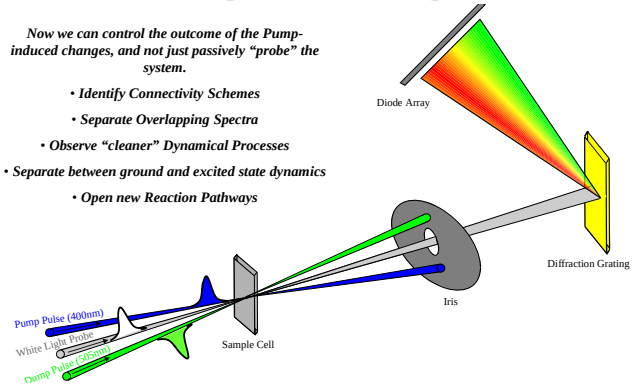


Pump-probe with a pair of probe pulses: one long (for narrow spectrum and good spectral resolution), and one short (for femtosecond time resolution).

Dispersed Multi-Pulse Experimental Setup

Now we can control the outcome of the Pump-induced changes, and not just passively "probe" the system.

- ***Identify Connectivity Schemes***
- ***Separate Overlapping Spectra***
- ***Observe "cleaner" Dynamical Processes***
- ***Separate between ground and excited state dynamics***
- ***Open new Reaction Pathways***



Dispersed Multi-Pulse Experimental Setup

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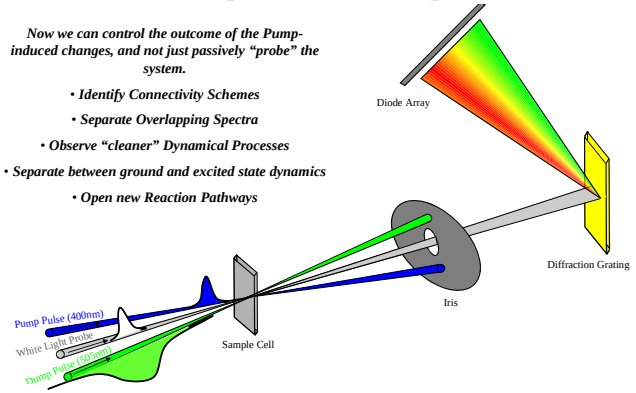
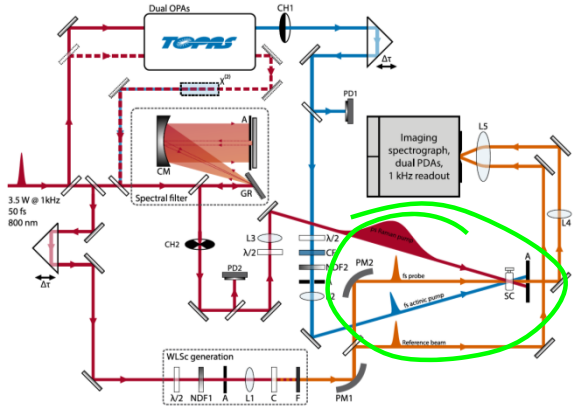
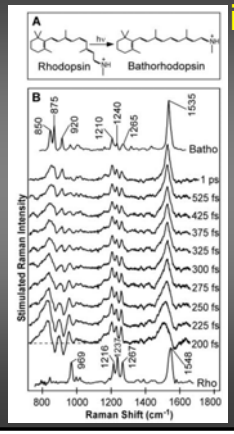
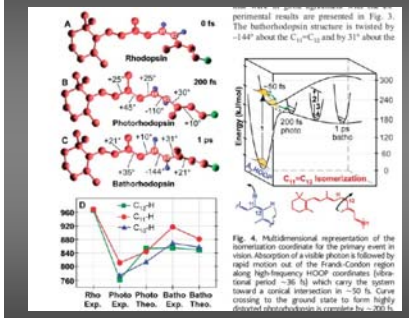


Setup for FSRS



Rhodopsin: vibrational signatures of isomerization



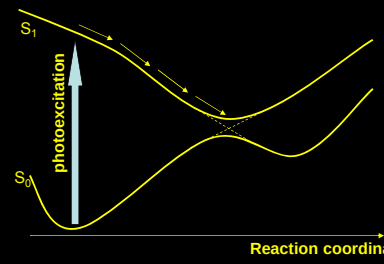


Kukura et al. Science 2005

Application: photochromism of indolo-benzoxazines

(spoiler alert: it's non-existent)

Bistable ground-state: sensitive to everything



- Solvatochromism
- Electrochromism
- Acidochromism
- Thermochromism
- etc.

Indolo-benzoxazines: new generation photochromic switches

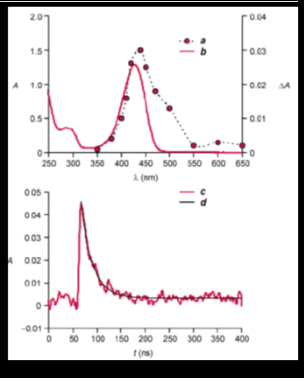
Tomasulo, M.; Sortino, S.; Raymo, F. i. M. *Organic Letters* **2005**, *7*, 1109.
Tomasulo, M.; Sortino, S.; White, A. J. P.; Raymo, F. M. *Journal of Organic Chemistry* **2005**, *70*, 8180. and at least 10 more papers on the same subject

Shachkus, A. A.; Degutis, J. A.; Urbonavichyus, A. G. *Khim. Geterotsikl. Soed.* **1989**, *5*, 672.

- Structure similar to spiropyrans;
- No triplet state – stable in aerobic conditions
- Fast thermal recyclization (25 ns)

Indolo-benzoxazines: ns photodynamics

Photoinduced absorption spectrum similar to that induced by the addition of strong base (Bu_4NOH)



Photochromism of indolo-benzoxazines

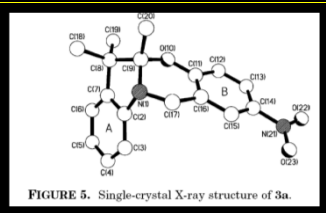
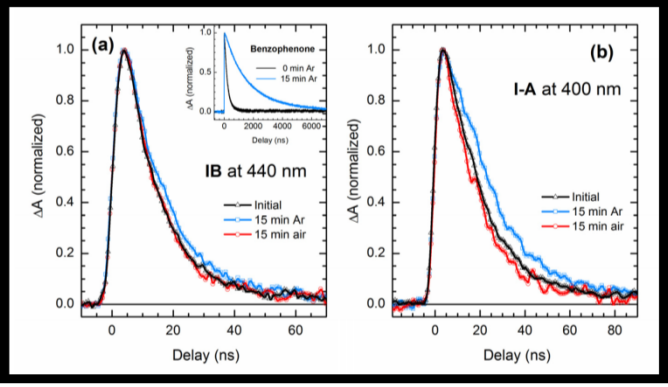


FIGURE 5. Single-crystal X-ray structure of 3a.

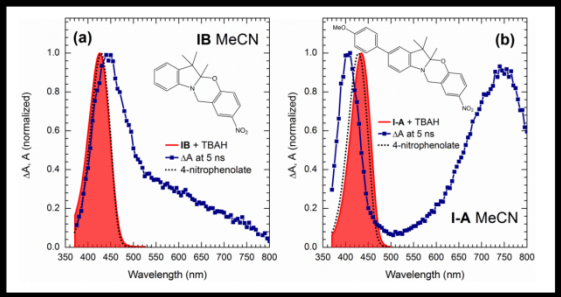
Prevaililing view: UV light induces bond cleavage, and produces a p-nitrophenolate chromophore responsible for the visible absorption.

Or is it?..

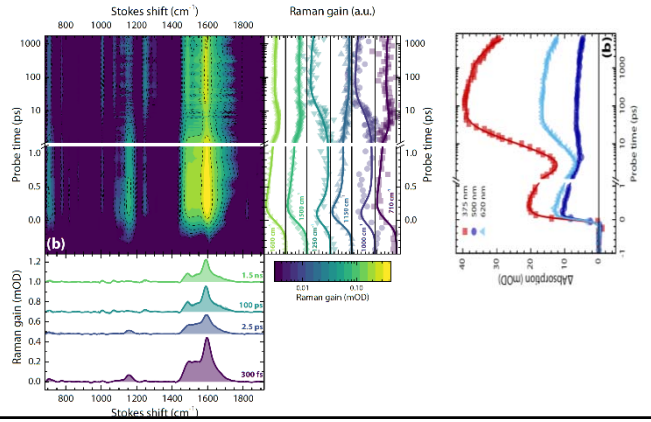
Oxygen effect on lifetime of "isomer"



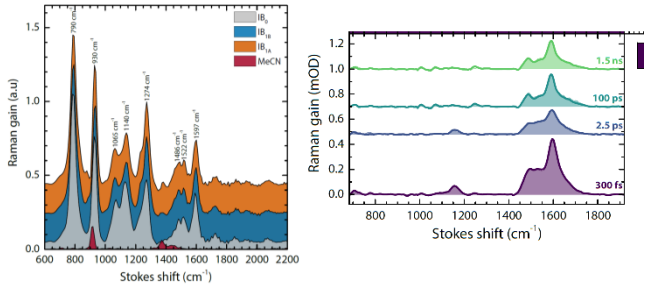
Absorption of open and closed forms



FSRS and optical pump-probe data



No match between optically and chemically induced Raman spectra!

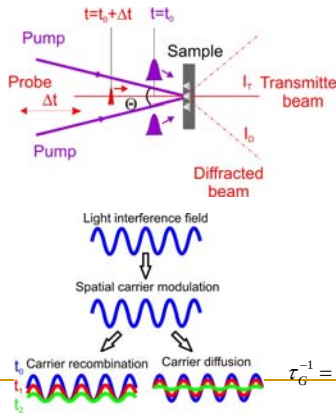


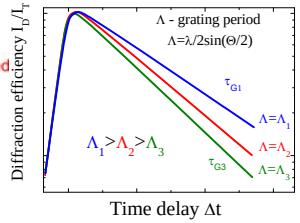
Therefore, definitely not photochromic. Pity.

Twist #3:

Coherent spectroscopies

Transient grating for diffusion length determination in semiconductors

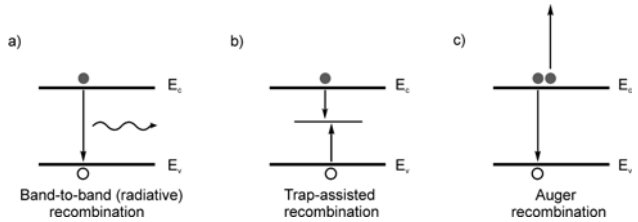




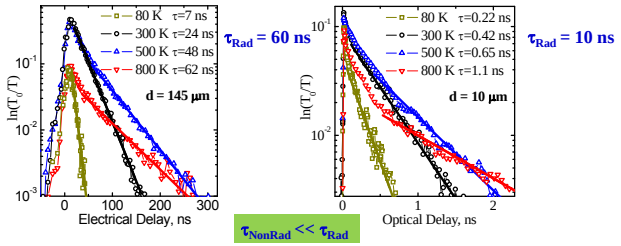
$$\frac{1}{\tau_G} = \frac{1}{\tau_R} + \frac{1}{\tau_D} = \frac{1}{\tau_R} + \frac{4\pi^2 D}{\Lambda^2}$$

$$\tau_G^{-1} = f(\Lambda^{-2}) \Rightarrow \tau_R, \mathrm{D} \Rightarrow L_D = \sqrt{\tau_R \mathrm{D}}$$

Recombination: Band-to-band (radiative), Shockley-Read-Hall (trap assisted), Auger recombination



Non-radiative recombination time in GaN



τ_{Rad} = 60 ns

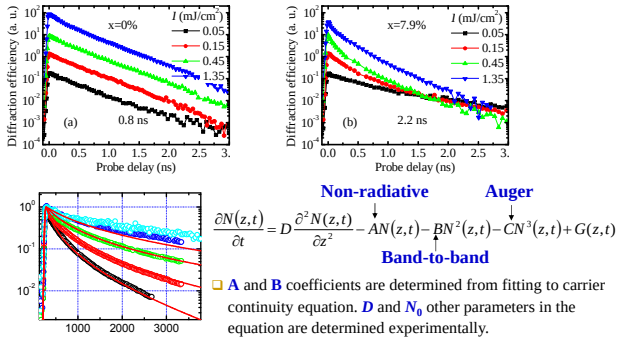
τ_{Rad} = 10 ns

$\tau_{NonRad} << \tau_{Rad}$

$$\frac{1}{\tau_R} = \frac{1}{\tau_{Rad}} + \frac{1}{\tau_{NonRad}} \qquad \tau_{Rad}(T, \Delta N) = \frac{1}{B(T)\Delta N} \qquad B(T) = 2 \times 10^{-11}\left(\frac{T}{300K}\right)^{-1.5}$$

- Non-radiative decay time τ_{NonRad} can be determined at low injection and/or after long decay time, when ΔN becomes small.

Recombination in $In_xGa_{1-x}N$ MQWs



Non-radiative **Auger**

$$\frac{\partial N(z,t)}{\partial t} = D\frac{\partial^2 N(z,t)}{\partial z^2} - AN(z,t) - BN^2(z,t) - CN^3(z,t) + G(z,t)$$

Band-to-band

- **A** and **B** coefficients are determined from fitting to carrier continuity equation. ***D*** and N_0 other parameters in the equation are determined experimentally.

Transient grating

- Combined with temperature dependence, can reveal the difusion coeffcients and recombination rates and modes in semiconductors.

More general case: three pulse echo

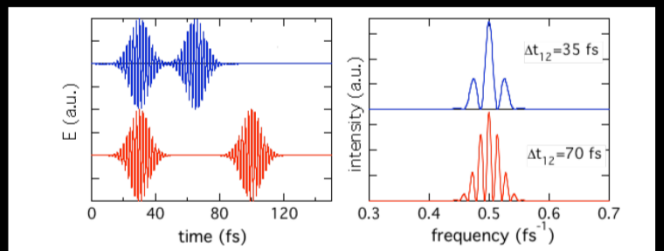


Figure 31: Electric field (left) and spectral intensity (right) associated with two 10 fs pulses separated by 35 and 70 fs.

Three pulse echo and inhomogeneous broadening

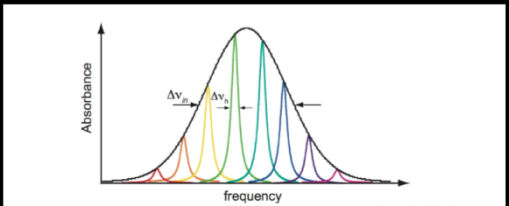


Figure 32: Homogeneous and inhomogeneous bandwidths.

Three pulse echo and inhomogeneous broadening

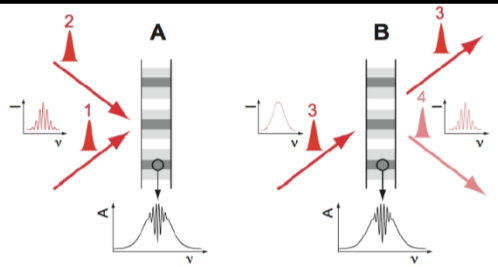
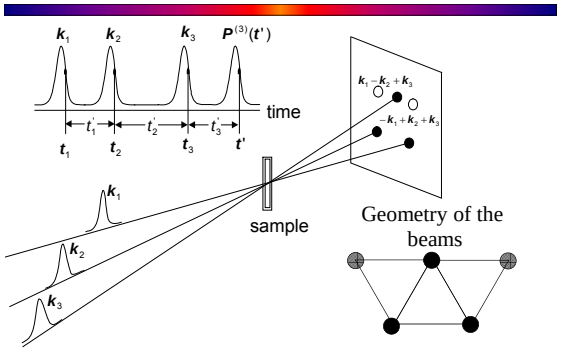
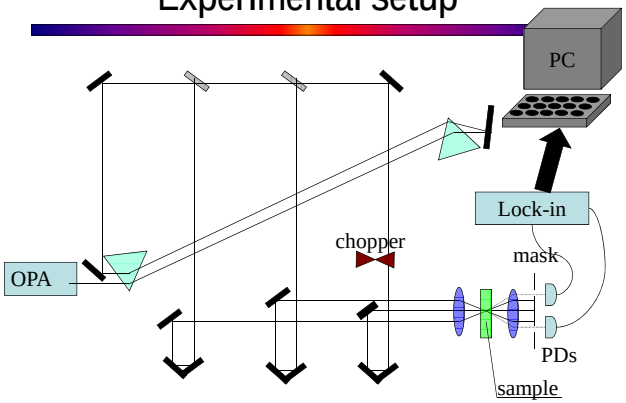


Figure 33: Transient grating description of the three-pulse photon echo technique.

Experiment scheme



Experimental setup



Three pulse echo

- The „writing“ pulses are separated in time, and their spectra are as wide as the absorption band of the sample. Shifted pulses result in frequency beating or *frequency grating.*
- The further the pulses – the finer the grating is.
- When too fine, it is very sensitive to spectral diffusion and signal quickly disappears (or, if inhomogeneous broadening is non-existent, the grating is not created to begin with;
- When too coarse, diffraction is weak
- Therefore, signal maximum is observed when the writing pulses are *SLIGHTLY* separated in time.

Frequency gratings

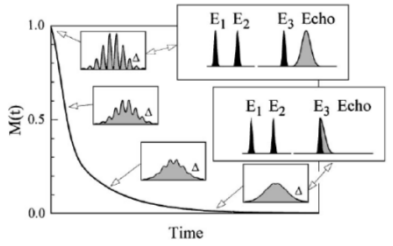
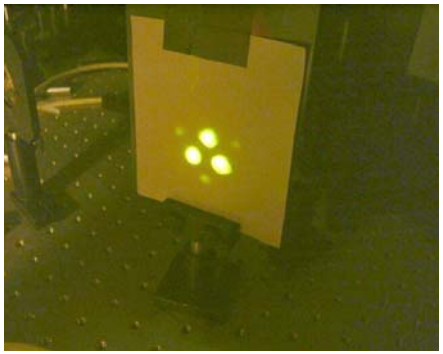
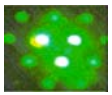


Figure 2 System-bath correlation function and associated decays of the frequency grating formed in the ground state. Δ denotes the frequency detuning from the optical transition. The excitation pulse sequence E_1-E_3 as well as the emitted signals are depicted for $M(t) = 1$ (inhomogeneous broadening) and $M(t) = 0$ (homogeneous broadening). Note that in the former case, the signal is delayed with respect to the last excitation pulse (photon echo), whereas in the latter case, the signal maximum coincides with the last excitation pulse (free induction decay).

How does it look?





What do we measure?

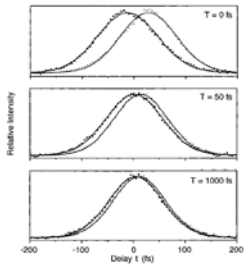
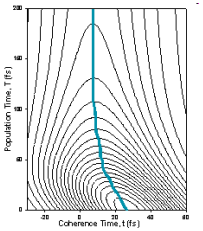


Figure 4. Examples of three 3PEPS scans (in the *t* dimension) obtained with α-subunit preparations at room temperature at T = 0, 50, and 1000 fs. The two traces represent the echo signals obtained from the two phase-matched directions. The traces are superimposed with fits to Gaussian line shapes, as determined by a nonlinear least-squares regression routine.



Peak shift decay follows the memory function of the bath coupled system

Polar dye in polar solvent

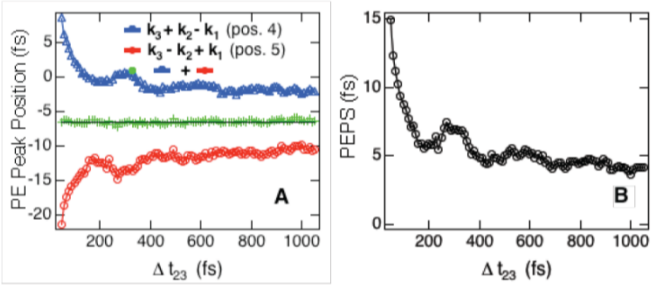
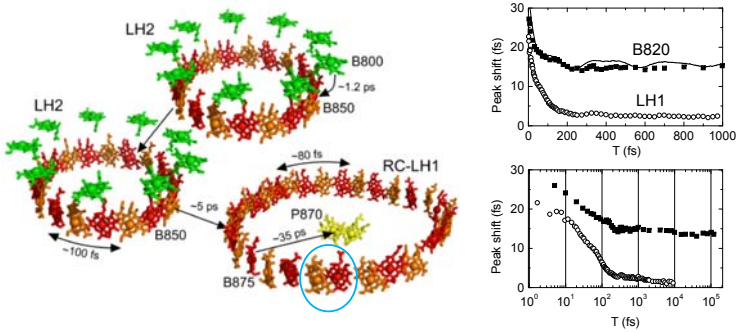


Figure 35: Peak position of the signal intensity recorded in the 4 and 5 position (A) and PEPS (B) measured with an ethanol solution of IR140.

3PEPS to monitor energy transfer



Problems

- After all this work, just one decaying curve is measured. Cannot produce too much science with just one curve ☹.
- Data interpretation requires the microscopic model (hamiltonian) of spectral diffusion.

2D electronic spectroscopy

- What if we measure not just the intensity of the photon echo, but the time dependence of the radiated EM field?
- We get 2D NMR analogue in optics, called two dimensional electronic spectroscopy (2DES).

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Phase-stabilized two-dimensional electronic spectroscopy

Tobias Brixner, Tomáš Mančal, Igor V. Stiopkin, and Graham R. Fleming[a)]
Department of Chemistry, University of California, Berkeley and Physical Biosciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

2D spectroscopy: plethora of pulses

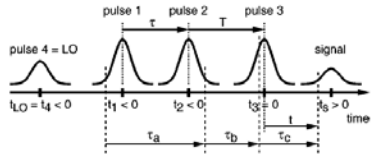


FIG. 1. Definition of time variables. Time zero is defined at the center of the third excitation pulse. The first two excitation pulses arrive at times $t_1<0$ and $t_2<0$, separated by the coherence time τ which is positive for the shown pulse order, and negative if pulse 2 arrives first. The population time $T>0$ is the separation between the second and third excitation pulse at $t_3=0$. Nonlinear third-order polarization at time t is induced by field interactions at times $\tau_a+\tau_b+\tau_c$, $\tau_b+\tau_c$, and τ_c earlier, which may occur somewhere under the excitation pulse envelopes. This leads to a free-induction decay and for inhomogeneously broadened systems, an additional photon echo signal is observed with an average arrival time t_s that is similar to the coherence time. The local oscillator (LO) used for heterodyned signal detection always arrives first at time t_4.

Experimental implementation

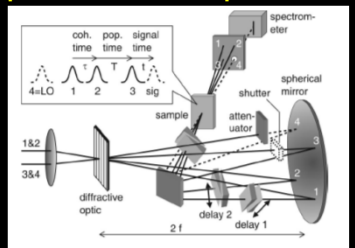


FIG. 2. Experimental setup. Two parallel beams of femtosecond laser pulses in the visible spectral region are focused by a lens onto a grating. The first diffraction orders emerge with high efficiency and provide the excitation pulses 1–3 as well as a local oscillator (4=LO) for heterodyne-detected three-pulse photon-echo electronic spectroscopy. A spherical mirror ($2f$ = 30 cm) creates an image of the pulse overlap in the sample cell via a plane folding mirror. The required time delays are provided with subwavelength precision by motor-controlled movable glass wedges. Full characterization of the nonlinear phase-matched signal field is carried out by spectral interferometry with the attenuated LO. An automated beam shutter is used for subtraction of scattering contributions. This diffractive-optics based setup is inherently phase-stabilized.

You can calibrate your λ/20 delays

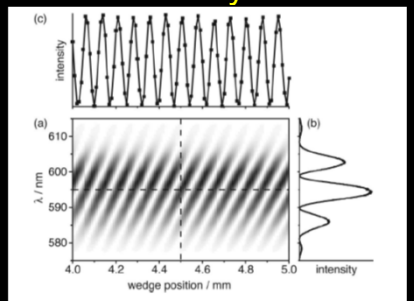
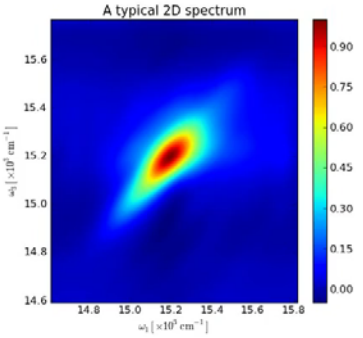


FIG. 3. Delay calibration by spectral interferometry. (a) Spectral interference patterns between pulses 1 and 2 are recorded in 10 μm steps by moving the glass wedge in arm 1. The cross section along the vertical dashed line shows (b) the spectral interference outside of the temporal pulse overlap, whereas the cross section along the horizontal dashed line delivers (c) the temporal oscillation for one particular wavelength. Counting these oscillations gives a precise calibration factor of wedge position vs time delay.

2D Electronic spectroscopy

- Can distinguish homogeneous and inhomogeneous broadening;
- Time resolution is not limited by spectral resolution on excitation scale;
- It's like many pump-probe experiments in one go!



2D electronic spectroscopy

- Requires detailed QM theory
- High coolness factor

2D electronic spectroscopy: what do we measure?

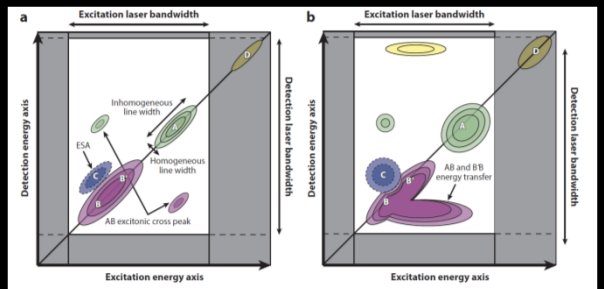


Figure 2

Schematic illustration of the information contained in absorptive two-dimensional Fourier transform spectra. The observed spectral range shown in the unshaded region is determined by the excitation and detection laser bandwidths. (*a*) The $T = 0$ correlation spectrum reveals homogeneous and inhomogeneous line widths, excitonic coupling, and excited state absorption features. (*b*) At $T > 0$, the broadening of peaks in the antidiagonal direction reflects spectral diffusion. The growth of cross peaks indicates energy transfer. The emergence of an entirely new peak at later waiting times, such as the B'D cross peak in panel *b*, represents the formation of a new product species, populated upon excitation of B', that absorbs at D. An example of such a process is the generation of a charge-separated state in the photosystem II reaction center (data shown in **Figure 4**).

If you are from Berkeley, you can publish anything you like!

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LETTERS

Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems

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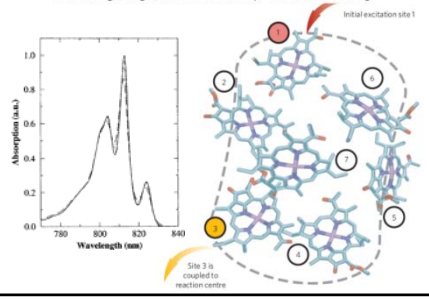
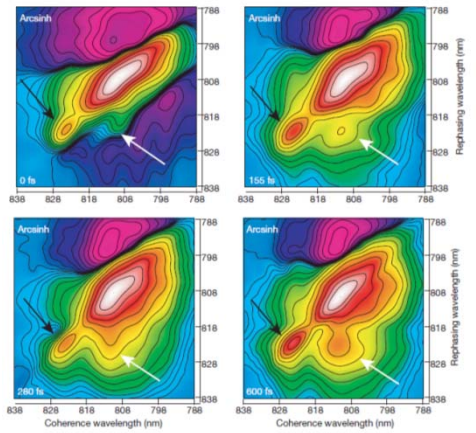


FMO complex, another light harvesting pigment protein complex.

Not much more than a bag of bacteriochlorophyll molecules with tight couplings.

Off-diagonal peak is oscillating!



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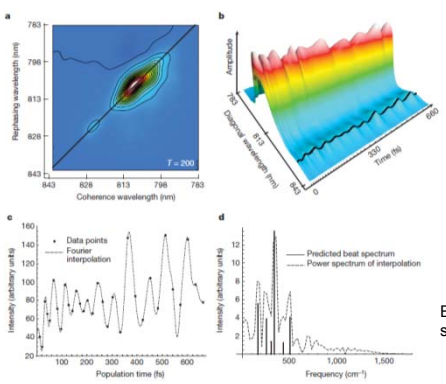


Figure 2 | Electronic coherence beating. a, A representative two-dimensional electronic spectrum with a line across the main diagonal peak. The amplitude along this diagonal line is plotted against population time in **b** with a black line covering the exciton 1 peak amplitude; the data are scaled by a smooth function effectively normalizing the data without affecting oscillations. A spline interpolation is used to connect the spectra; the times at which spectra were taken are denoted by tick marks along the time axis. **c,** The amplitude of the peak corresponding to exciton 1 shown with a dotted Fourier interpolation. **d,** The power spectrum of the Fourier interpolation in **c** is plotted with the theoretical spectrum showing beats between exciton 1 and excitons 2–7.

Electronic coherences should dephase in <50 fs

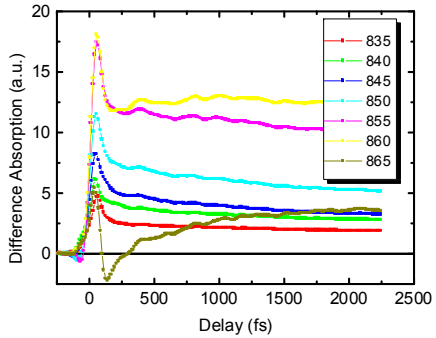
This 'wavelike' energy transfer started the now fashionable (hopefully, not for long) field of quantum biology…

My never published data from 2000

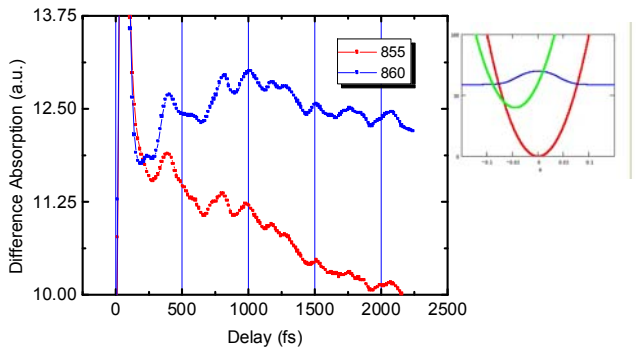
Coherent response of nucleic subsystem to the excitation.

- Good old Rps. Acidophila;
- Pump-probe at 77K;
- Purpose: observe how the nuclei of BChl molecules respond to the electronic excitation.

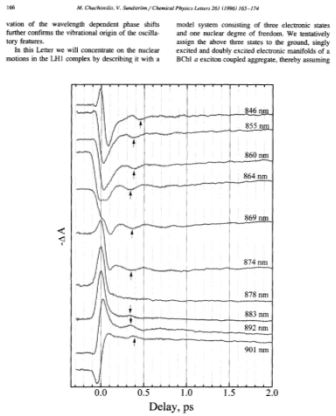
Kinetics at various wavelengths (77K)



It is not noise!



4 years earlier (1996)



Instead of conclusions…

Time-resolved spectroscopy comes in a lot of different guises and is used in different fields for understanding the quantum-mechanical functioning of light sensitive matter.

Used wisely, it is a powerful box of tools for investigating nature.

Used bravely, it gets you papers in Nature (sometimes even despite the science being wrong).