Do We Live in a Quantum World? — A New "Twist"

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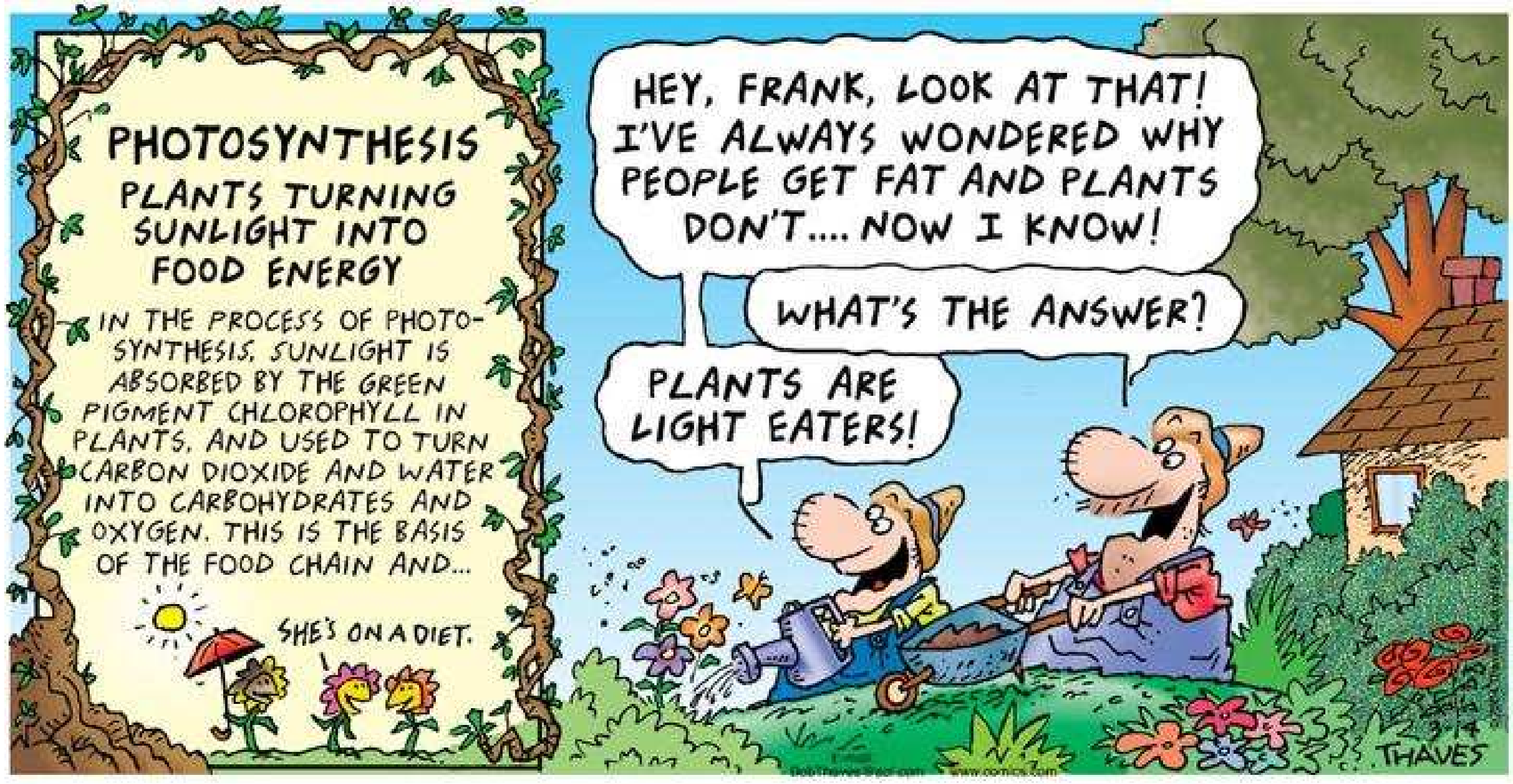
In the beginning….



V. Prokhorenko

Fundamental issue: how well is the biosystem optimized to this "light food" ??

Quantum Coherence and Biology

Tenet: Biological systems (at the molecular level) have evolved to control the transition state region

Barrier Crossings (transition state processes)

occur over atomic length scales $\Rightarrow$ wave properties of matter become significant

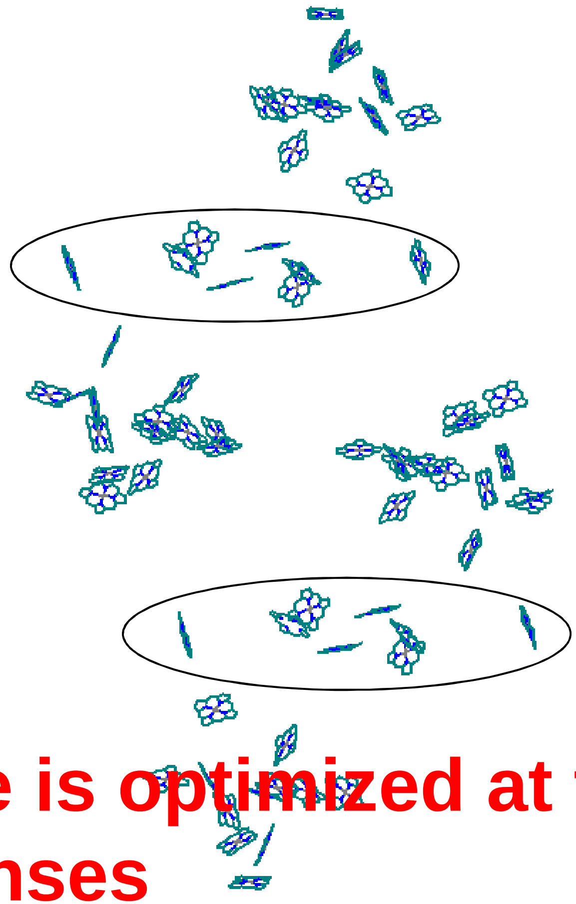
Has Nature evolved to even exploit phase?

Coherence properties of waves require an interferometer to measure $\Rightarrow$ Coherent Control $\equiv$ Molecular Frame of Reference Interferometer

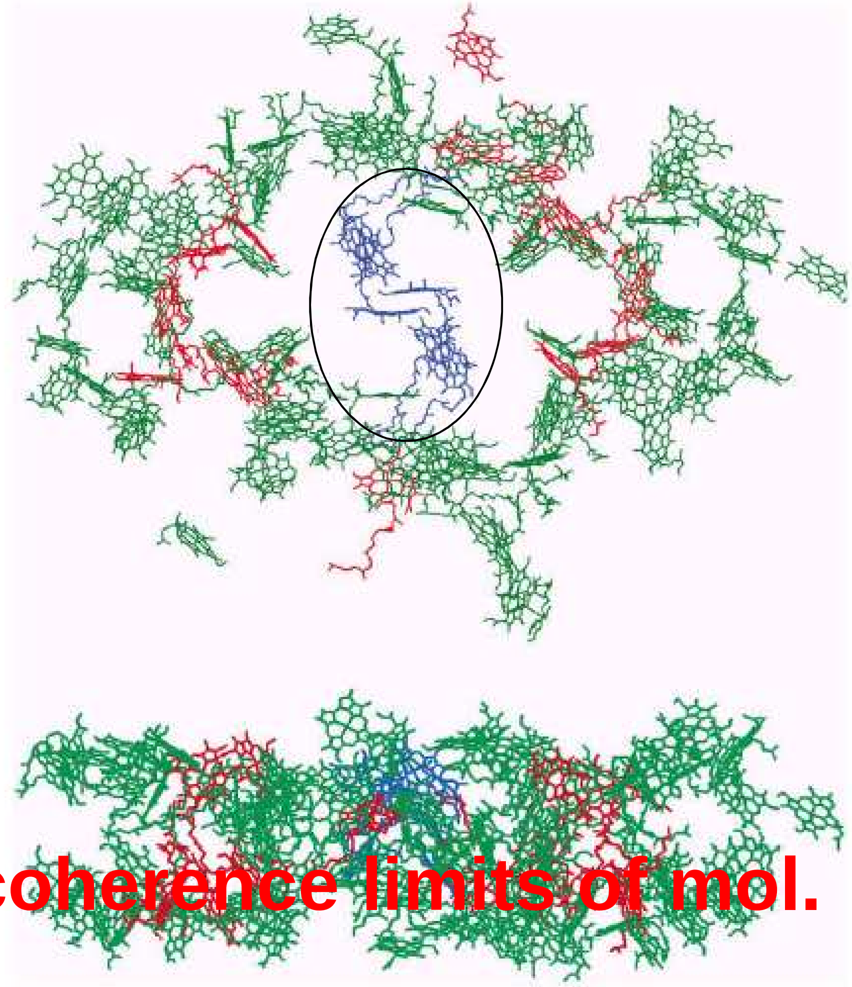
Intrepid Surfer Analogy

•**Structures of PS II and PS I (protein not shown)**

X-Ray structure of Photosystem II from *S. elongatus* with 3.8 Å resolution, file # 1FE1 in PDB.
A. Zouni et al. *Nature*, 409, 739 (2001).

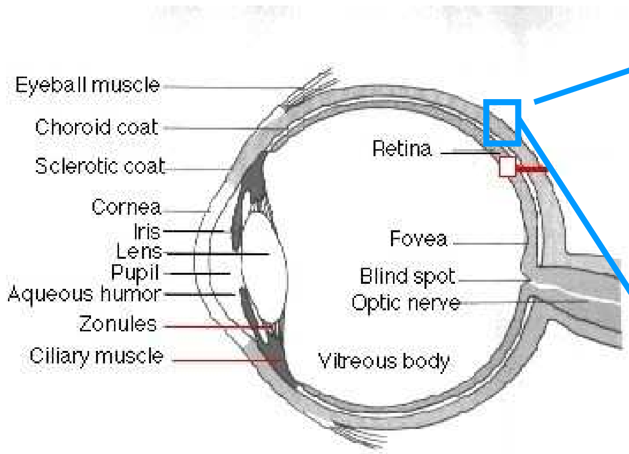


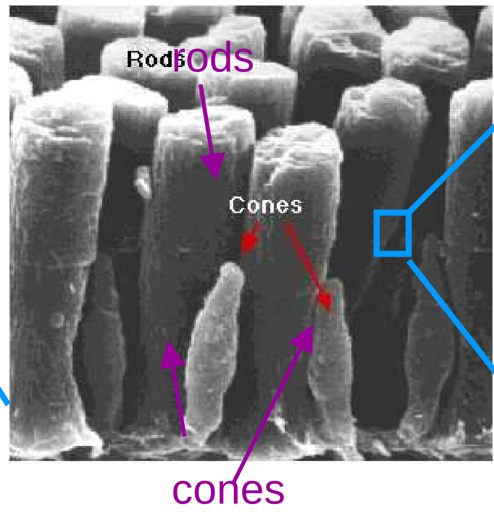
X-Ray structure of Photosystem I from *S. elongatus* with 2.5 Å resolution, file # 1JBO in PDB.
P. Jordan et al. *Nature*, 411, 909 (2001).



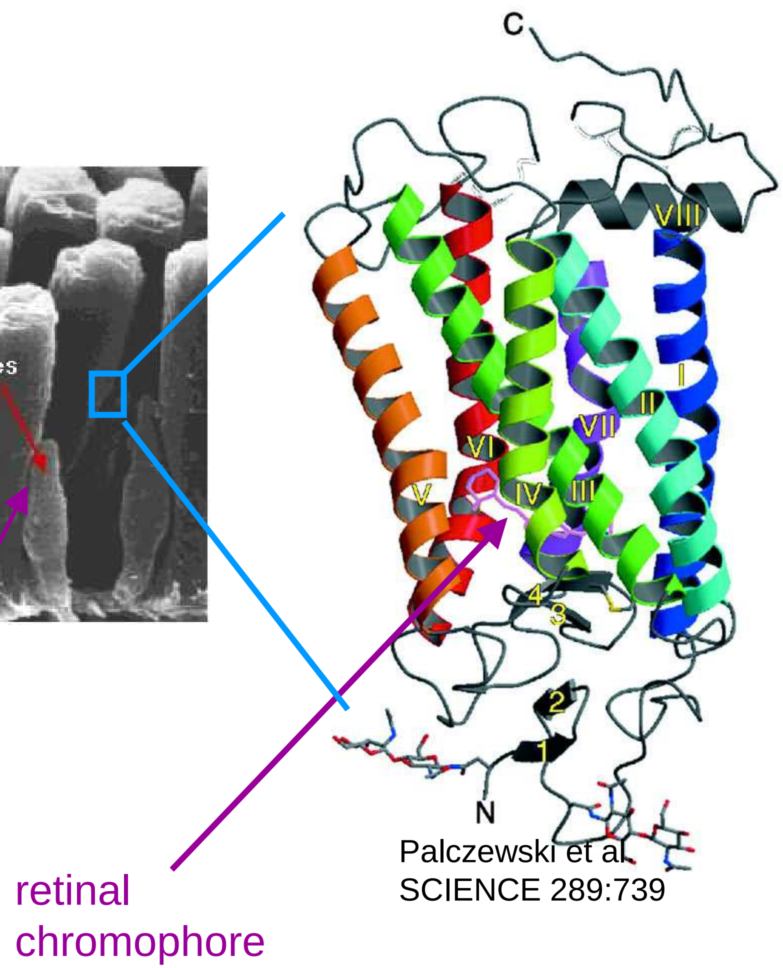
Nature is optimized at the coherence limits of mol. responses

The Dream – Controlling Isomerization in Rhodopsin





http://users.rcn.com/jkimball.ma.ultranet/BiologyPages/V/Vision.html



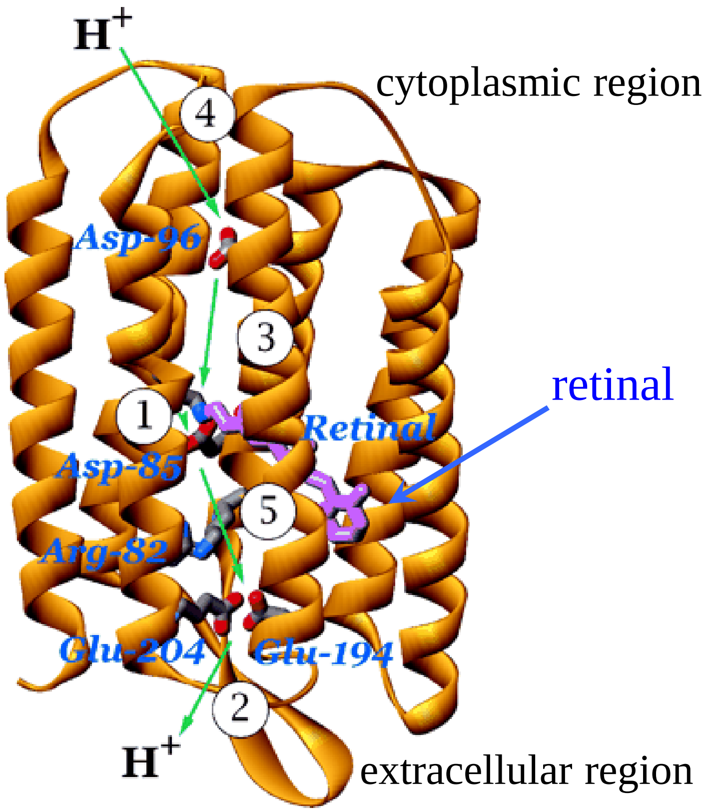
Palczewski et al.
SCIENCE 289:739

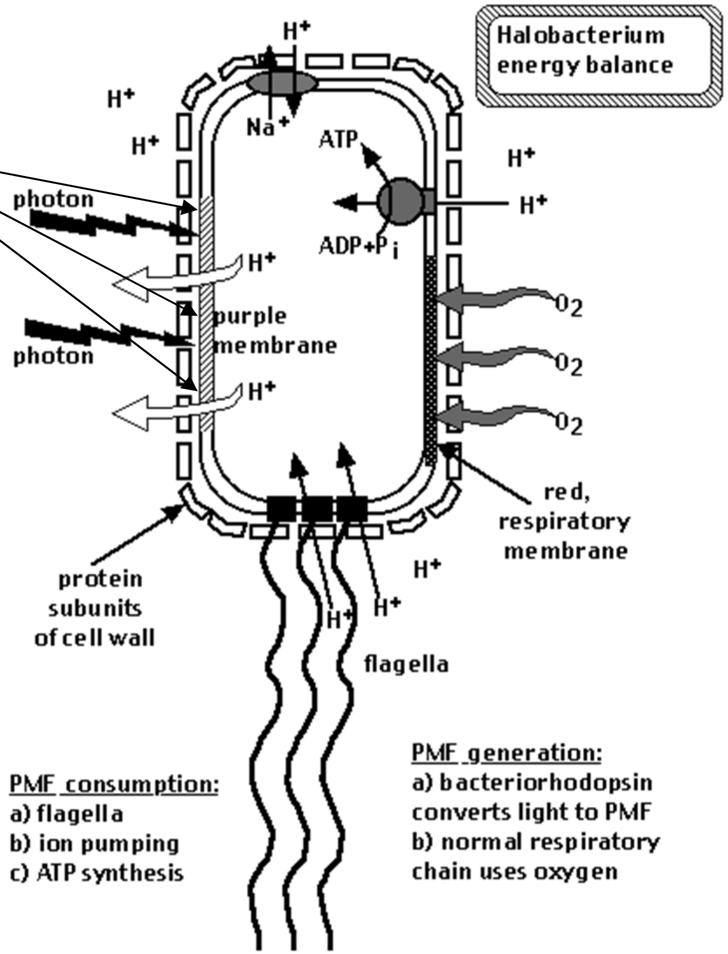
Ideal System: Biologically Relevant Photoinduced Function THAT is fast enough to compete with Quantum Decoherence ⇒ **Must Demonstrate under Weak Field Control**

Q. Wang, R. Schonlein, L. Peteaunu, R. Mathies, C. Shank, Science 1994, 266, 422

Bacteriorhodopsin-a Precursor to Rhodopsin

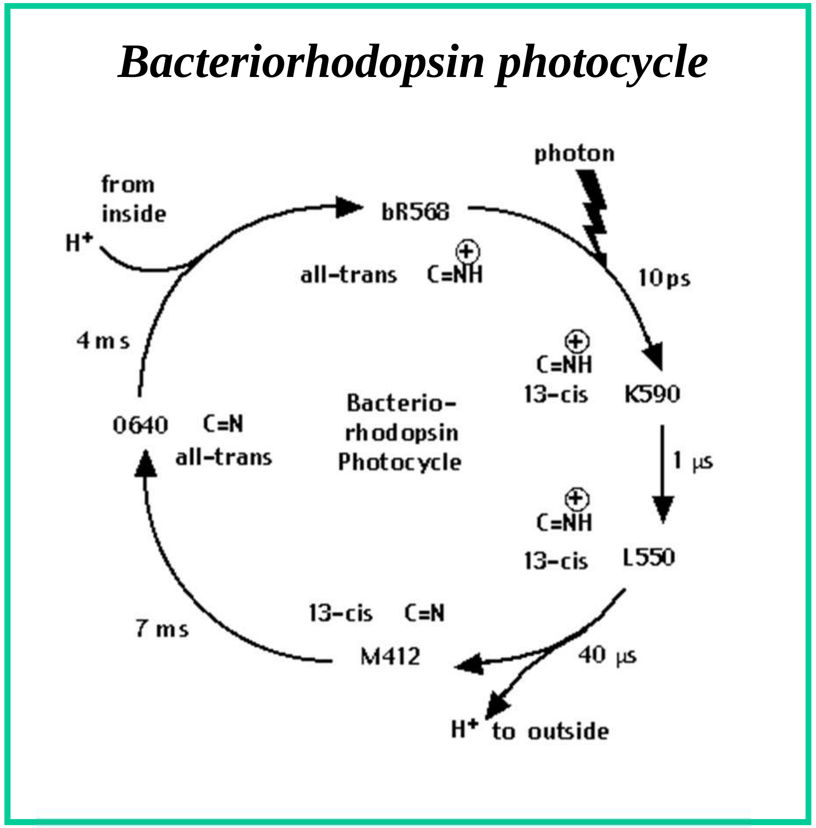
bacteriorhodopsins
are sitting in purple
membrane

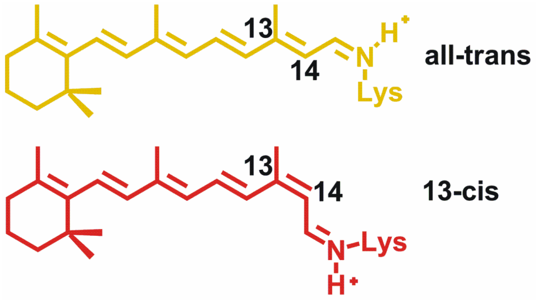


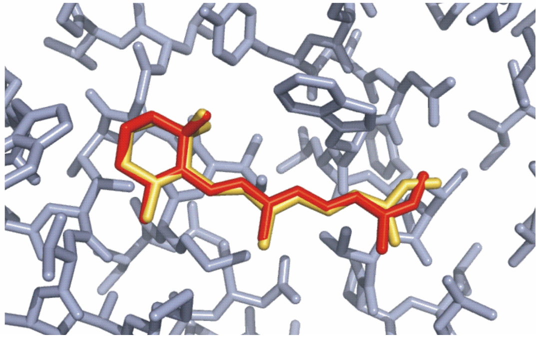


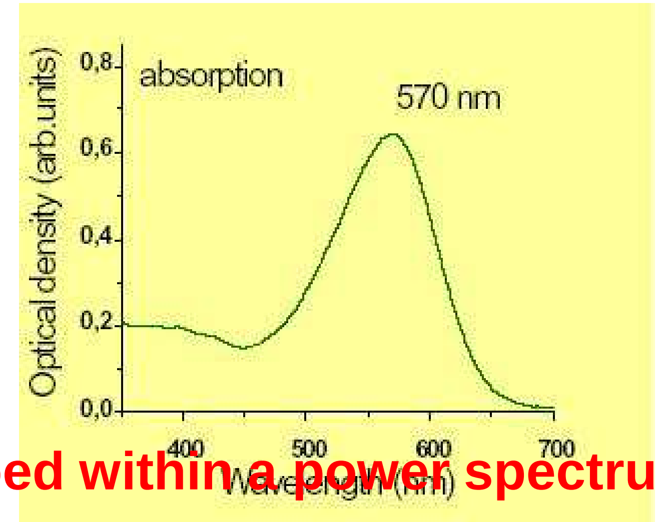
http://www.science.siu.edu/microbiolog/micr425/Halobacteria96

•Bacteriorhodopsin – the smallest chameleon in Nature









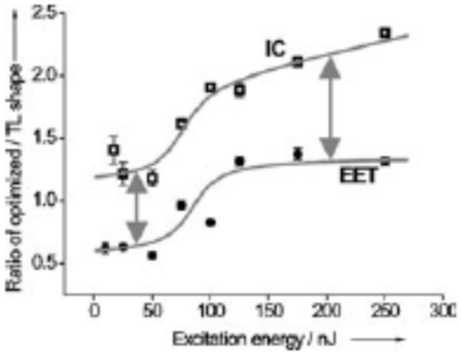
http://www.science.siu.edu/microbiolog/micr425/Halobacteria96

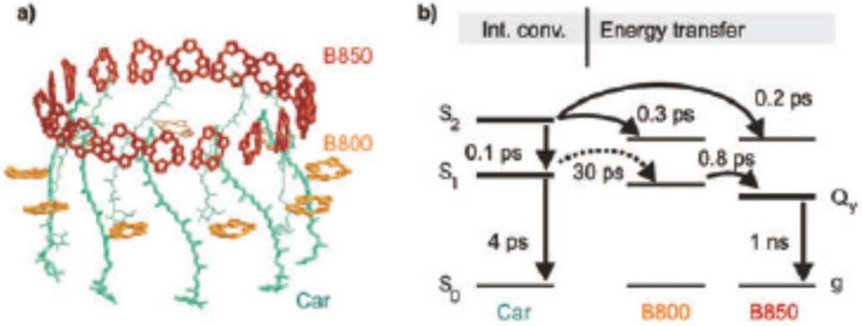
all-trans form: light-adapted ground state →

Efficiency of isomerization ~ 65%

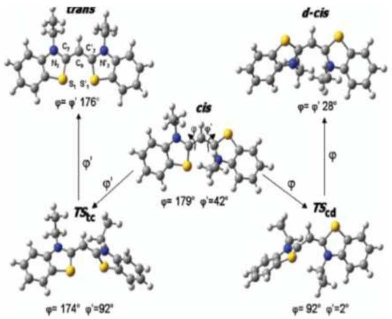
⇒ Reaction Dynamics can be described within a power spectrum re: dominant mode couplings

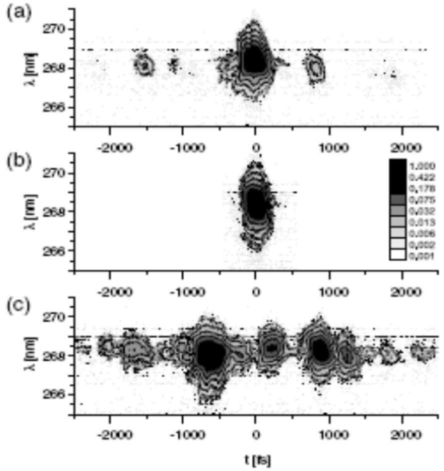
Relevant Experimental Work





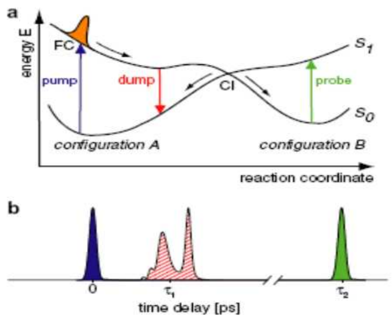
Wohlleben et al. ChemPhysChem, 6, 850, 2005 (Herek and Motkus groups)





Nuemberger et al. JCP, 125, 044512 (2006)/Vogt et al PRL 2005

Vogt et al. CPL 433, 211 (2006)

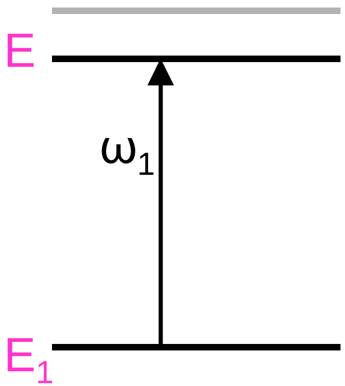


⇒ Degree of Control Increases under Strong Field/High Intensity Conditions

Coherent Control in the Weak Field Limit

CLOSED QUANTUM SYSTEMS

-no coupling to bath

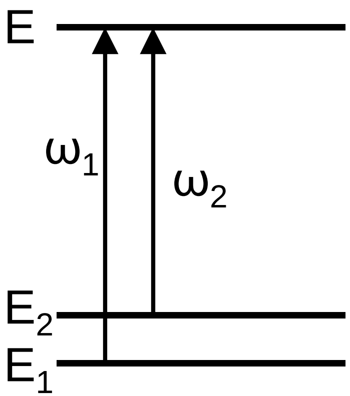


Single state case:
1 eigenstate ⇒ 1 pathway
- no interference

→ no control

M. Shapiro and P. Brumer

bichromatic control

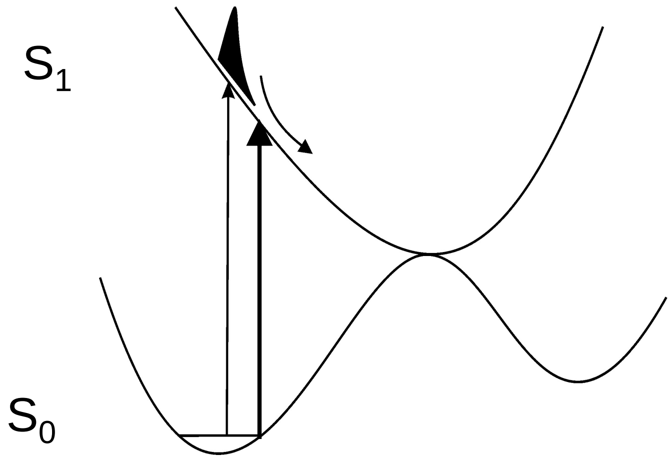


bichromic case: 2 pathways
- linear
- fixed phase leads to interference

→ coherent control

OPEN QUANTUM SYSTEMS

-coupling to bath, or surroundings

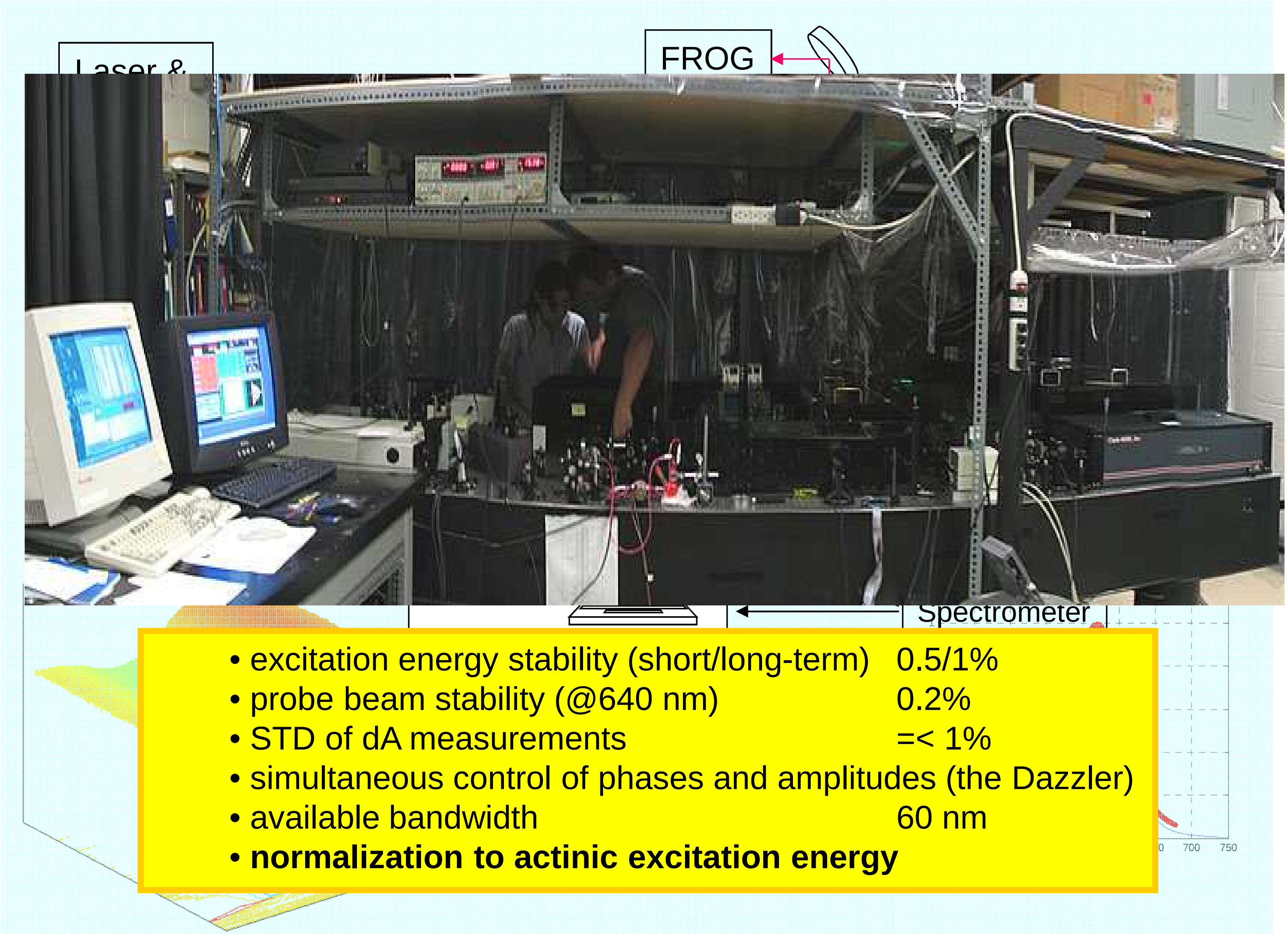


- several pathways
- interference at CI
- phase sensitive relaxation/dissipation to bath

→coherent control

Prokhorenko et al., Chem. Phys. (2007)

Coherent control setup

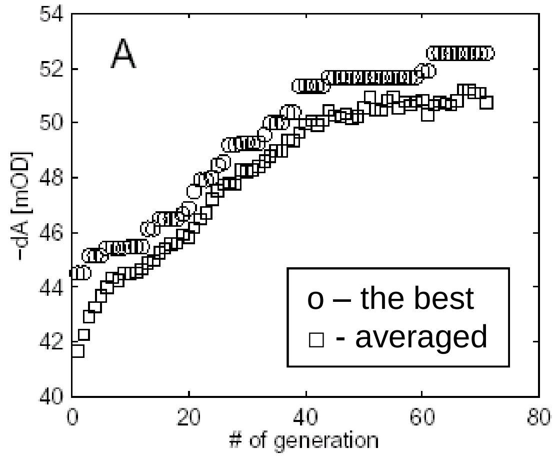


- excitation energy stability (short/long-term) 0.5/1%
- probe beam stability (@640 nm) 0.2%
- STD of dA measurements =< 1%
- simultaneous control of phases and amplitudes (the Dazzler)
- available bandwidth 60 nm
- **normalization to actinic excitation energy**

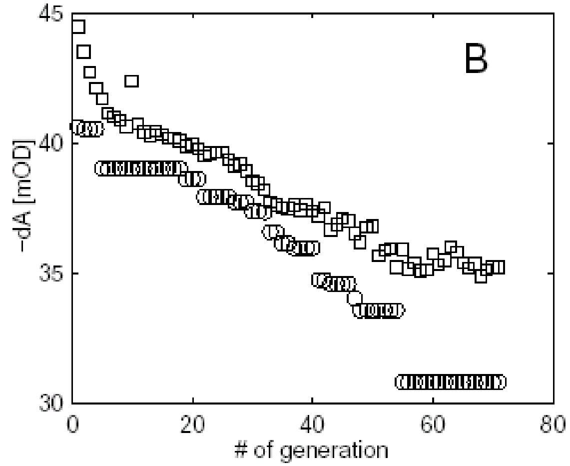
Enhancement and suppressing of S1 - population

Conditions: 5 ps delay after excitation; 5 nJ, MA, RT, @ 580 nm

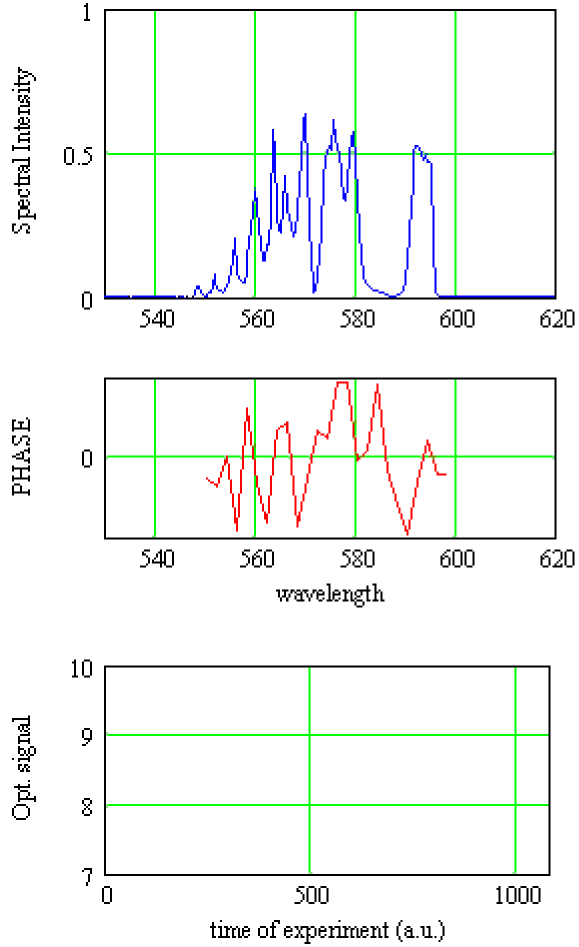
maximization



minimization



how it works:
an *optimization* experiment

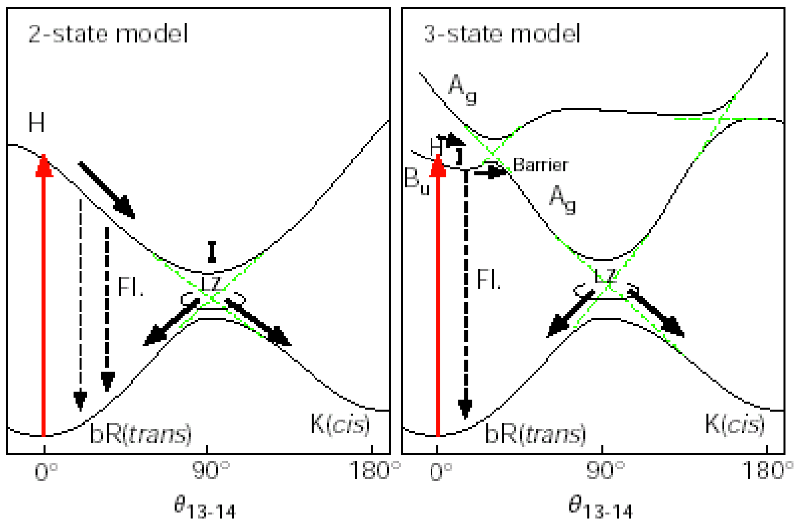


⇒ Coherent Control of Population Transfer is possible in Weak Field Limit

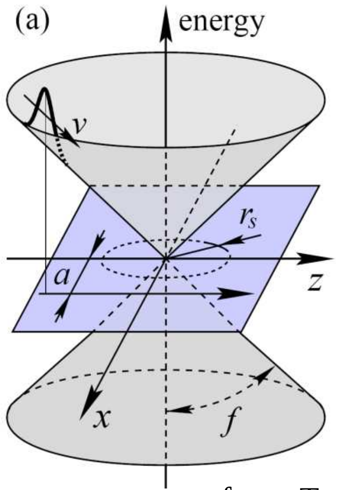
Coherent Control of Retinal Photoisomerization*
— Quantum Control of a Biological Function

GOAL

- Control isomerization efficiency under these restrictions:
  a) weak field excitation (within **linear response** regime)
  b) **fixed number of absorbed photons** per laser shot



from: Kobyashi et al., Nature, v. 414 (2001)



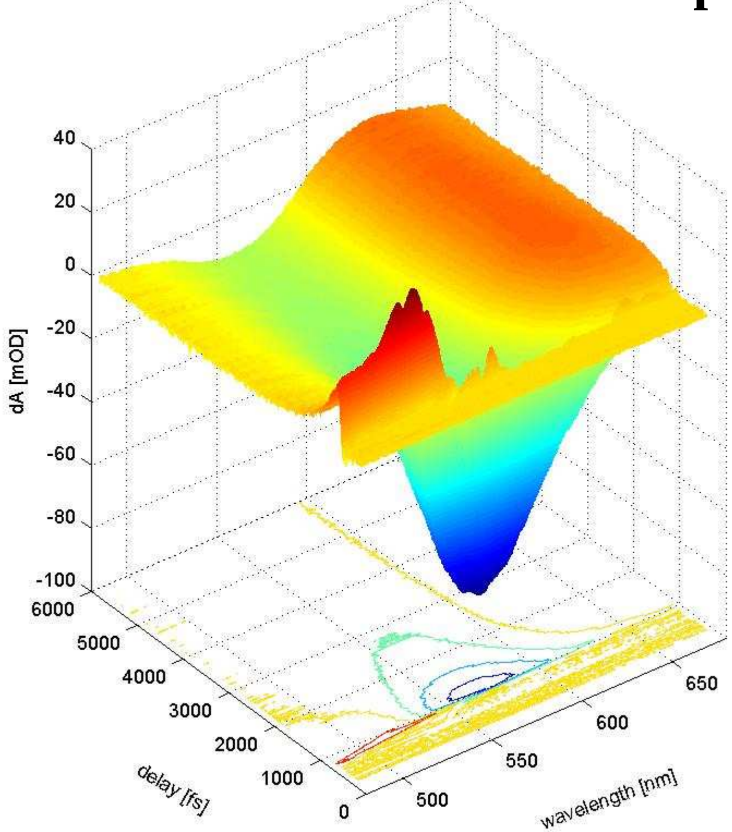
from: Tretyak et al., PRL 95 2005

Isomerization in terms of wave packet language: a ballistic passing of wave packet from excited state through conical intersection point (given as an “aperture”) to 13-*cis* ground state

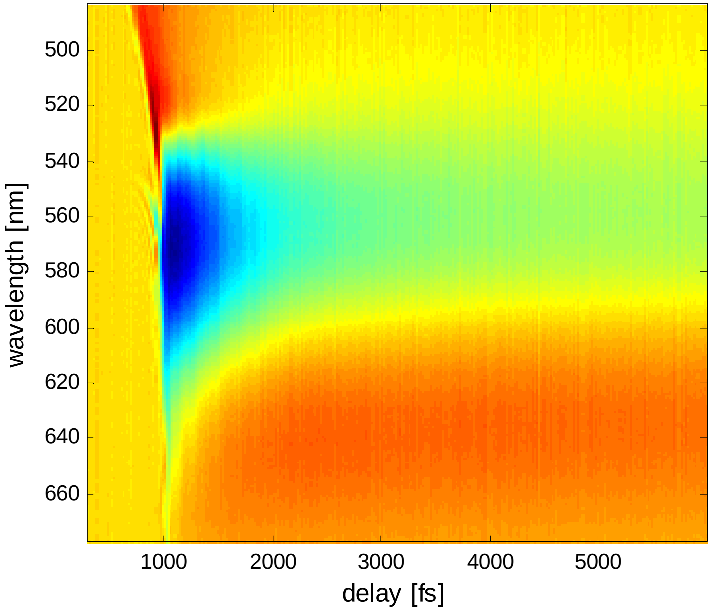
*V. Prokhorenko et al. Science **2006**, 313: 1257

Primary steps in bacteriorhodopsin photocycle: pump – probe kinetics of all *trans* → 13 *cis* isomerization

Excitation with 20 fs laser pulse



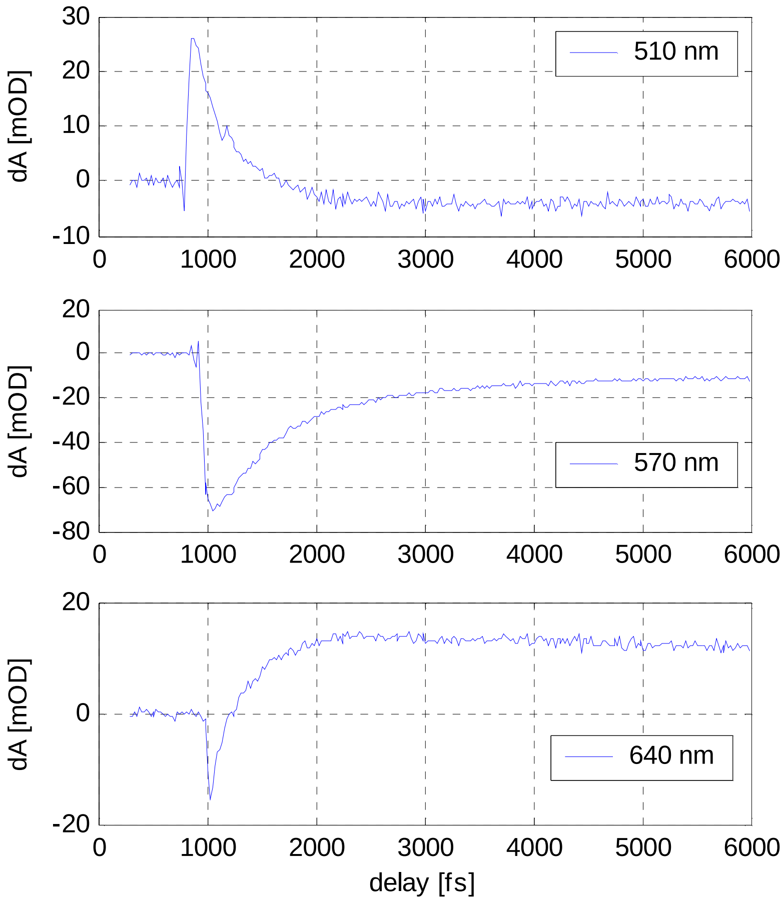
2D-plot



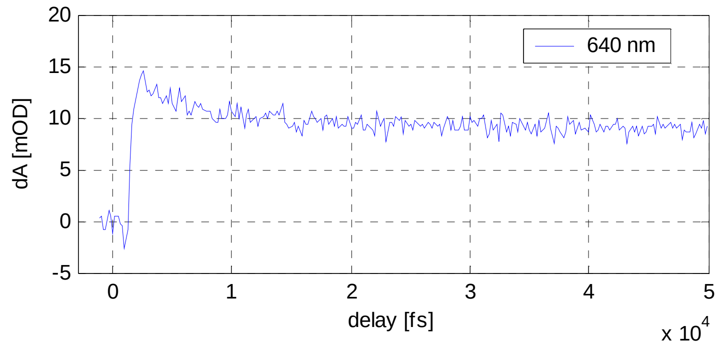
Samples:

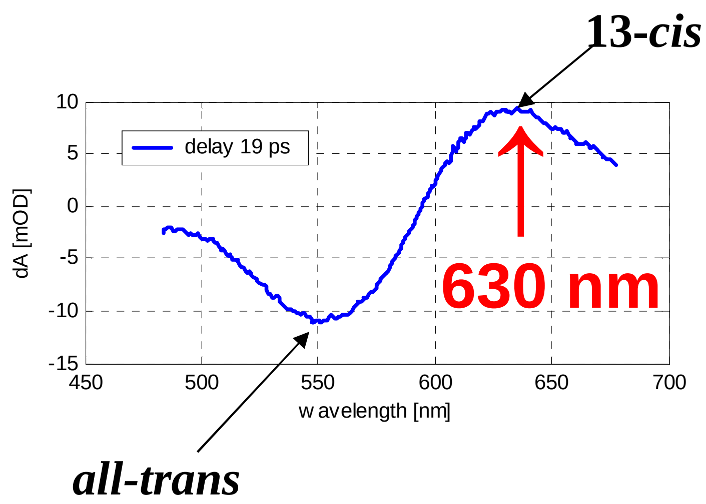
- buffer NaCl + Phosph (pH = 6.5)
- OD in max. absorbance 0.8; flow cell 400 um
- room temperature, MA measuring conditions, cut-off filter (probe beam)
- light-adapted (before experiments and continuously during measurements
- sonicated direct before measurements (for suppressing of scattering)

Decay traces at different wavelengths



Scan in delay window 50 ps: shows some decay of ***cis*** – form during ~ few ps



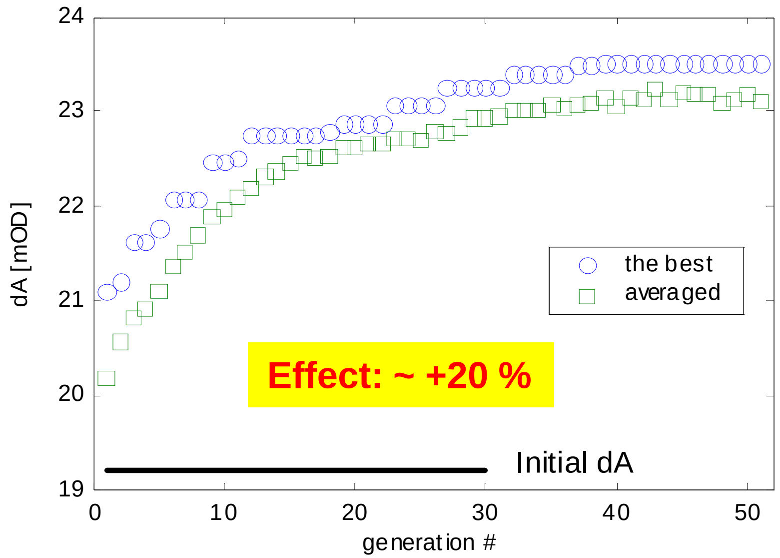


Growth of *cis* – form occurs within τ ~ 450 fs

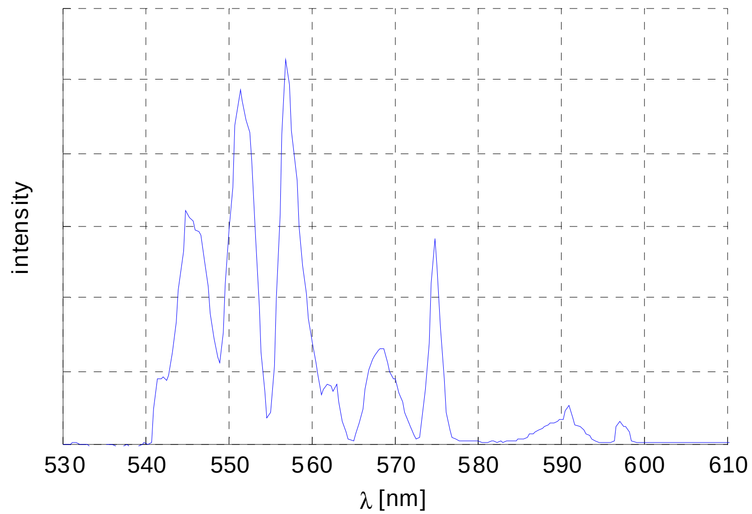
Optimization experiment: enhancement of *cis* – yield using pulse shaping

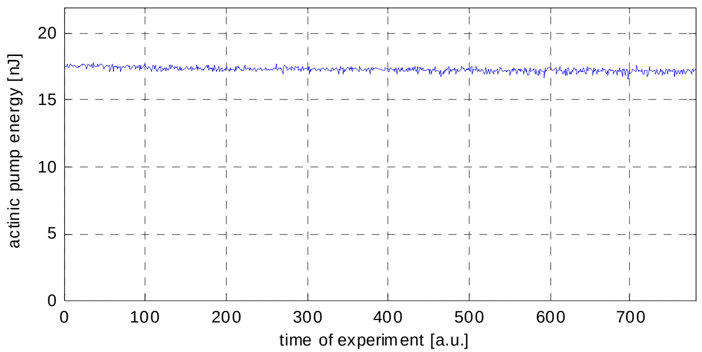
Pump: 16 nJ, delay 20 ps after excitation; observation @ 630 nm (IF 10 nm)
Spectrum: controlled within 60 nm (540 – 600 nm), step 2 nm, 32 levels

Optimization process: 50 generations



Spectrum of optimal pulse

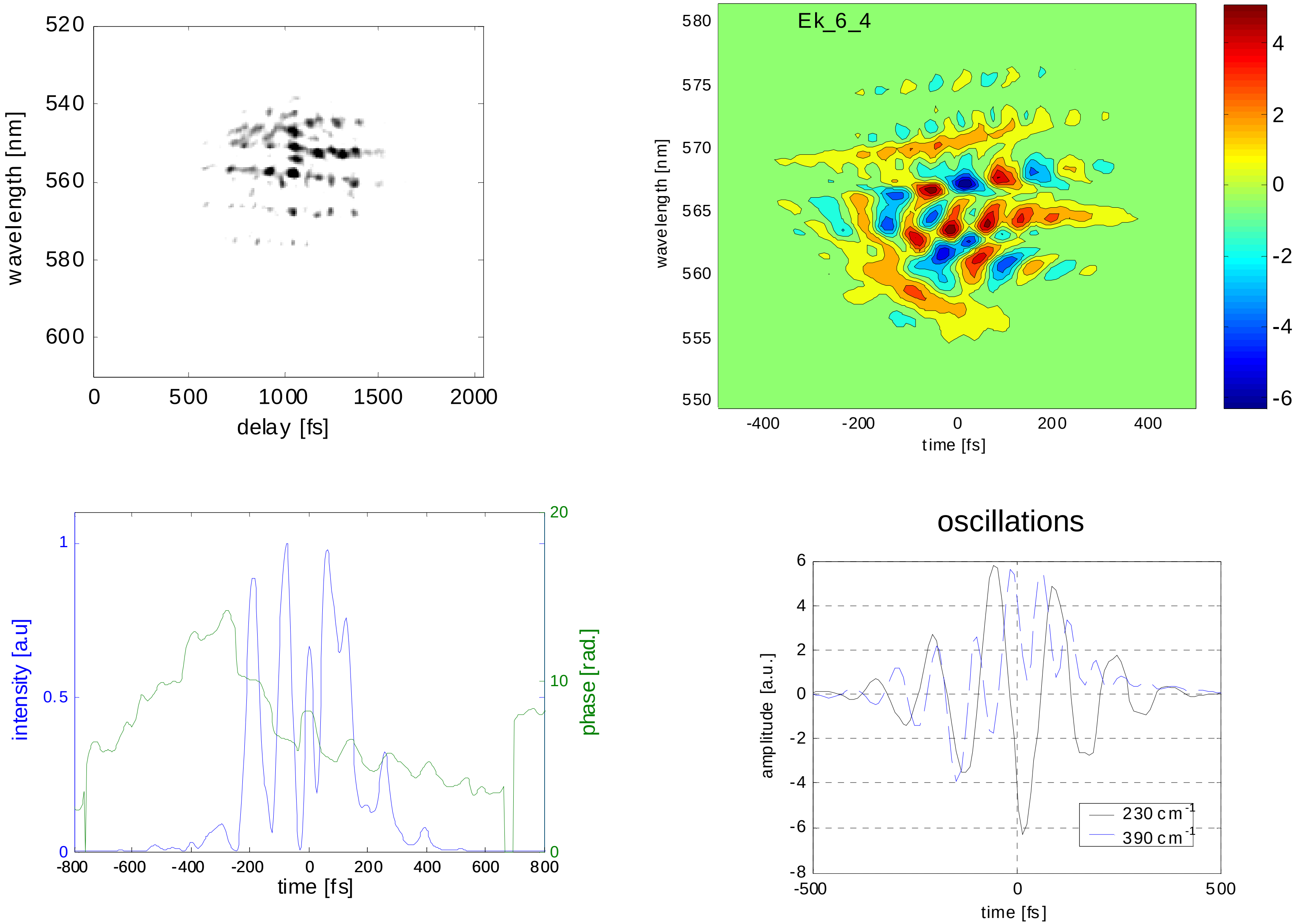




Spacing between main components:
~ 7.1 nm (+/- 0.9 nm)
➔ ~ 210 cm-1

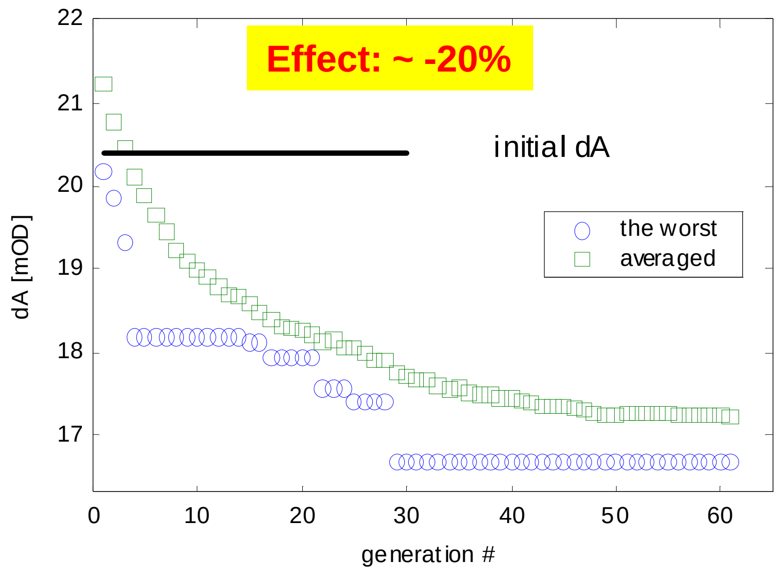
V. Prokhorenko et al. Science **2006**, 313: 1257

Temporal structure of the optimal pulse: FROG data and Wigner plot

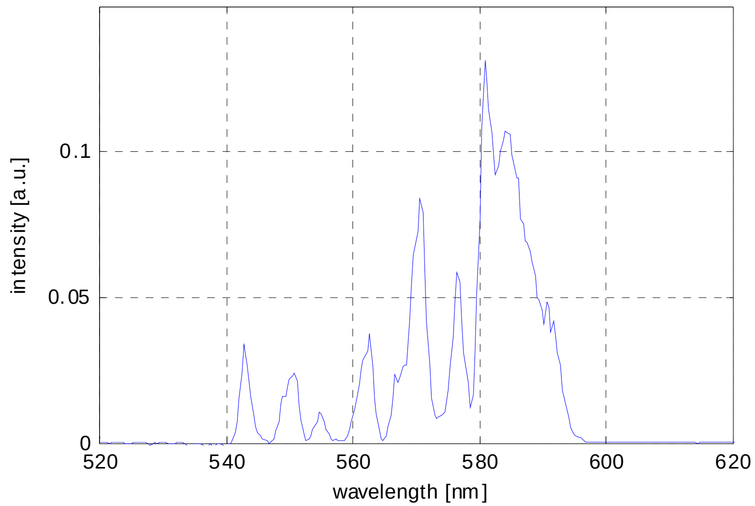


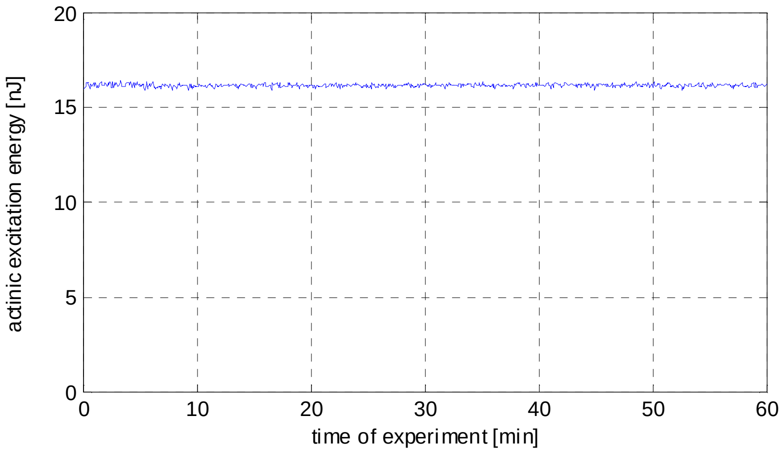
Minimization experiment: suppressing *cis-* yield using shaped pulses

Anti-optimization process: 60 generations

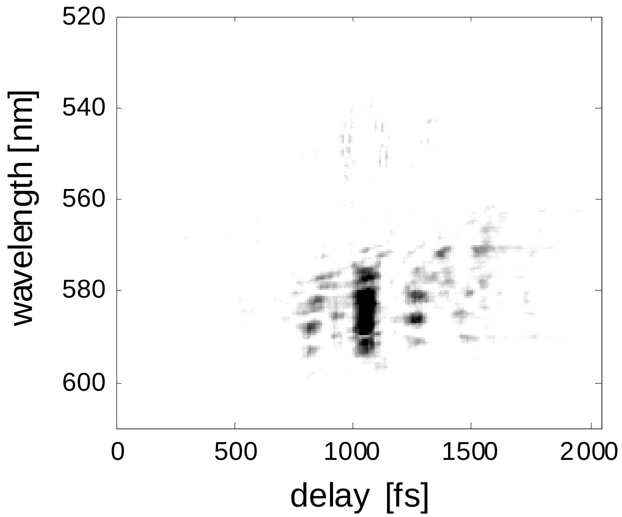


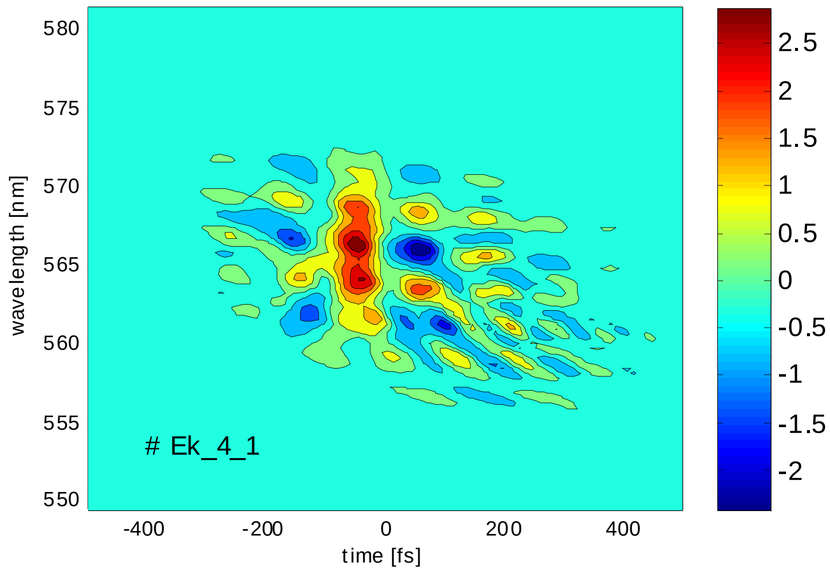
Spectrum of anti-optimal pulse

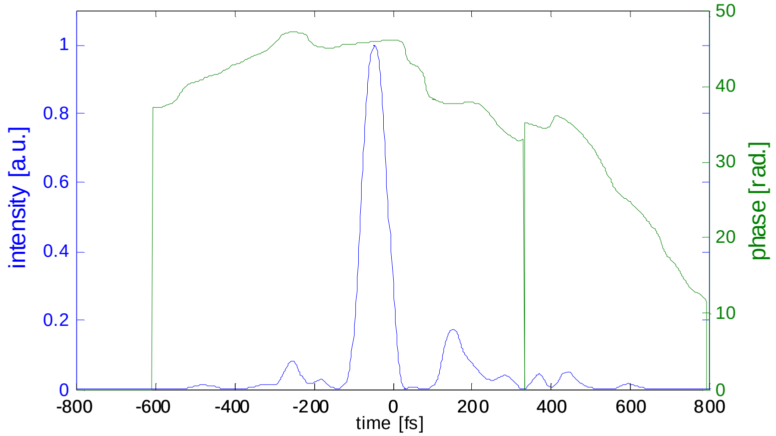




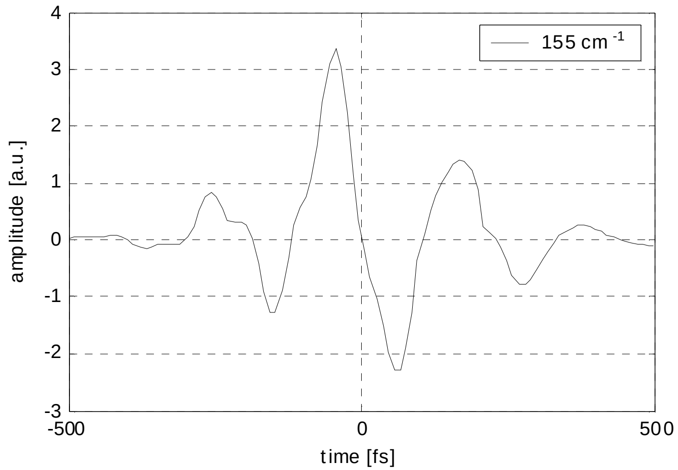
Temporal structure of the anti-optimal pulse



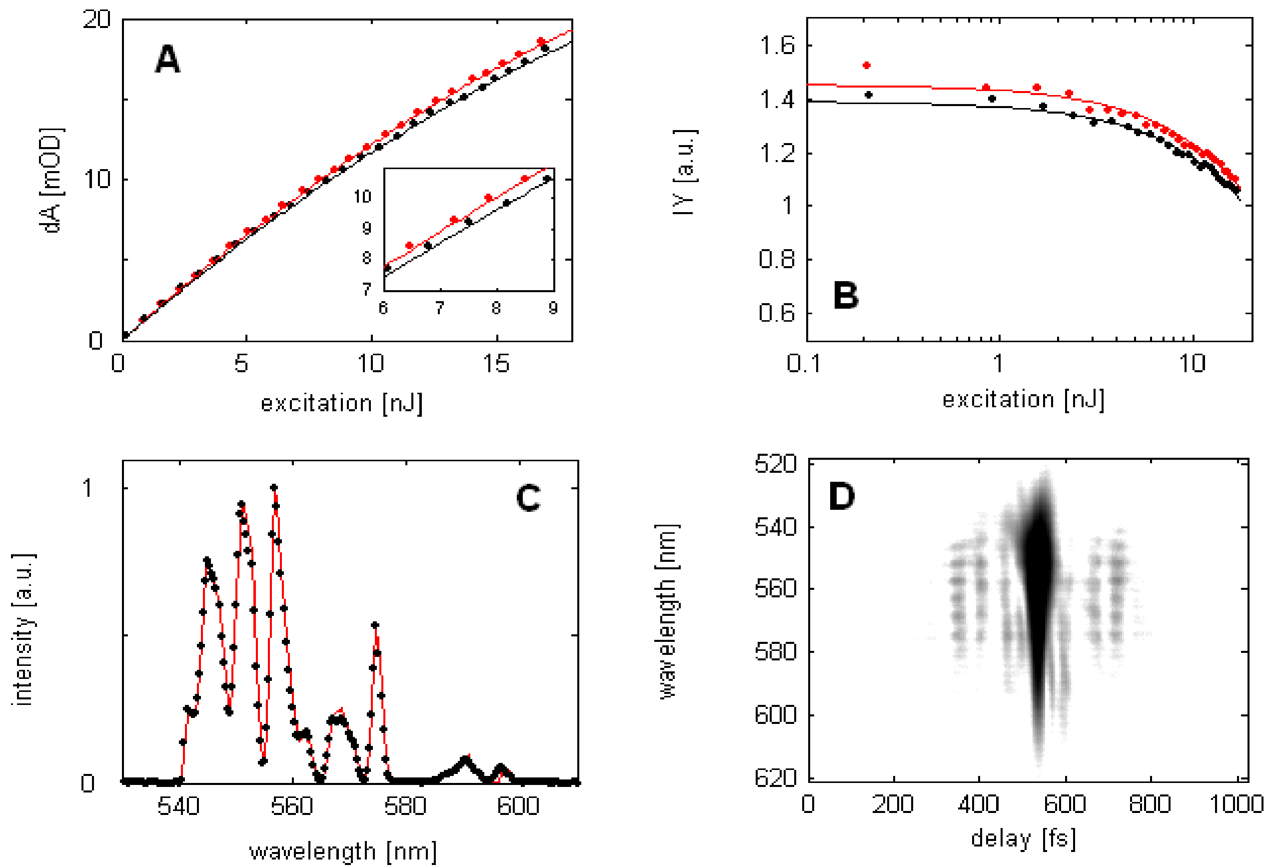




oscillations



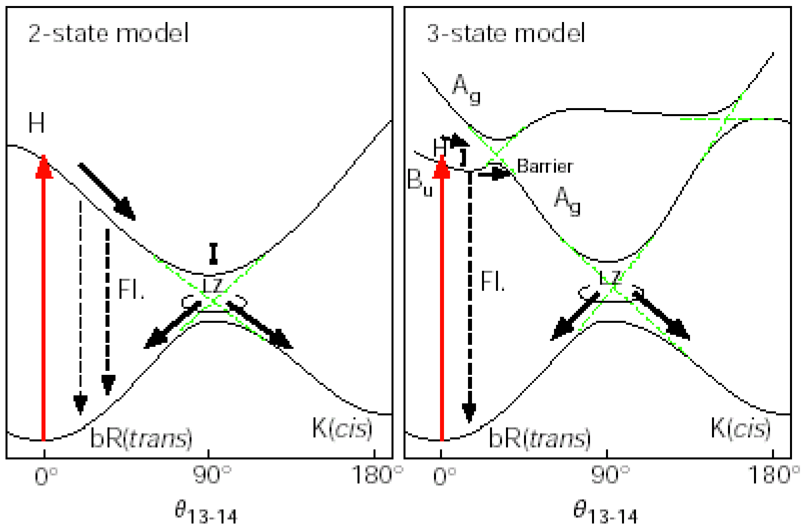
Phase dependence: optimal pulse with - and without phase modulation

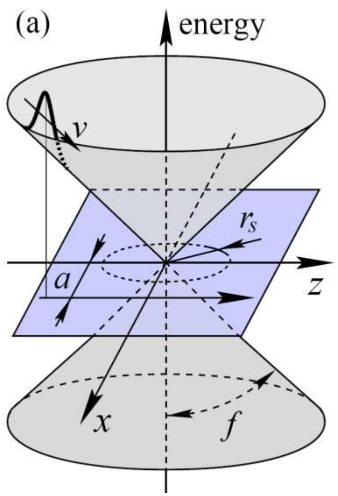


Spectra of pulses - identical **FROG of pulse with flat phase**

⇒ Coherent Control….Quantum Coherence persists along reaction coordinate

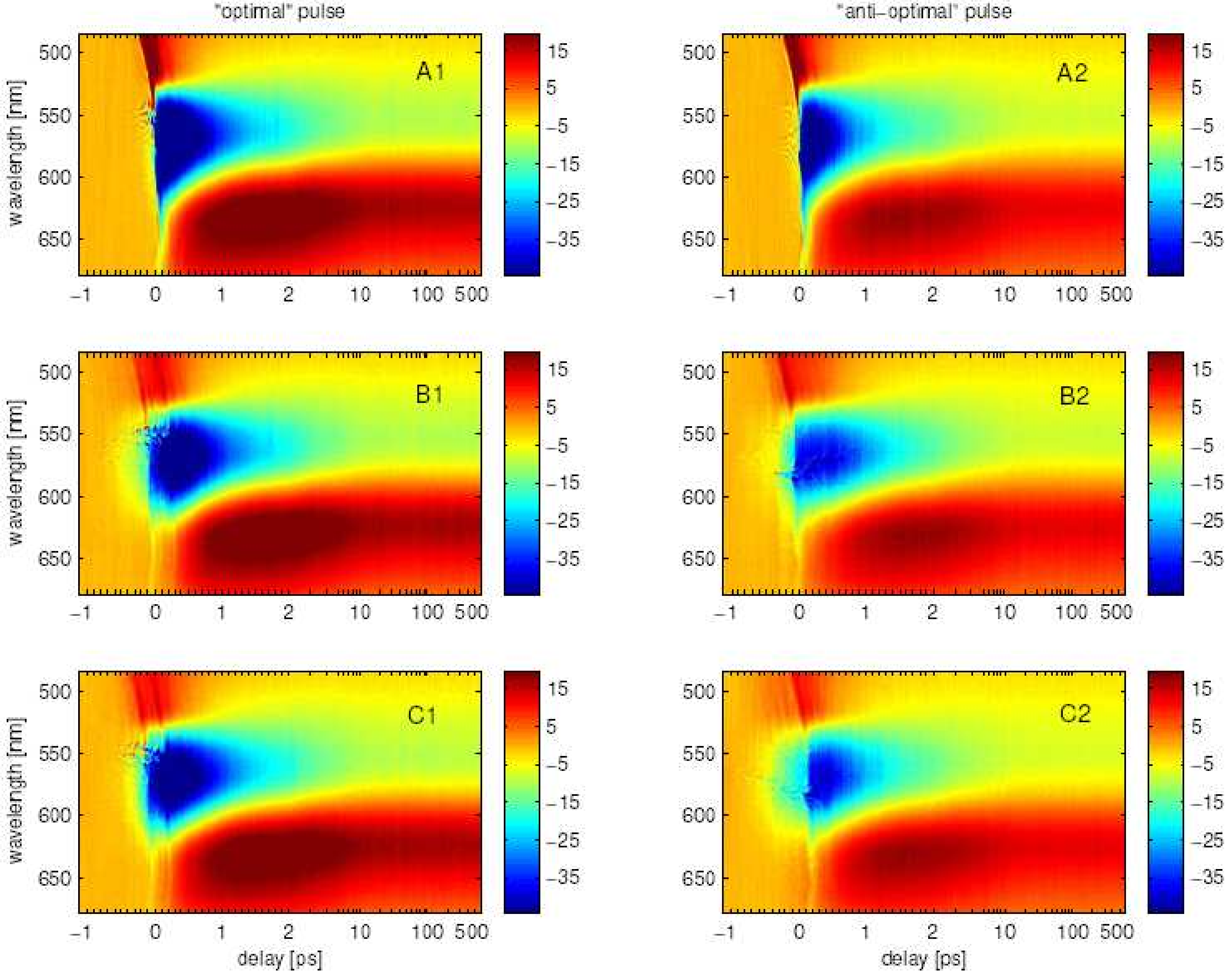
Phase Dependence: Reaction Dynamics





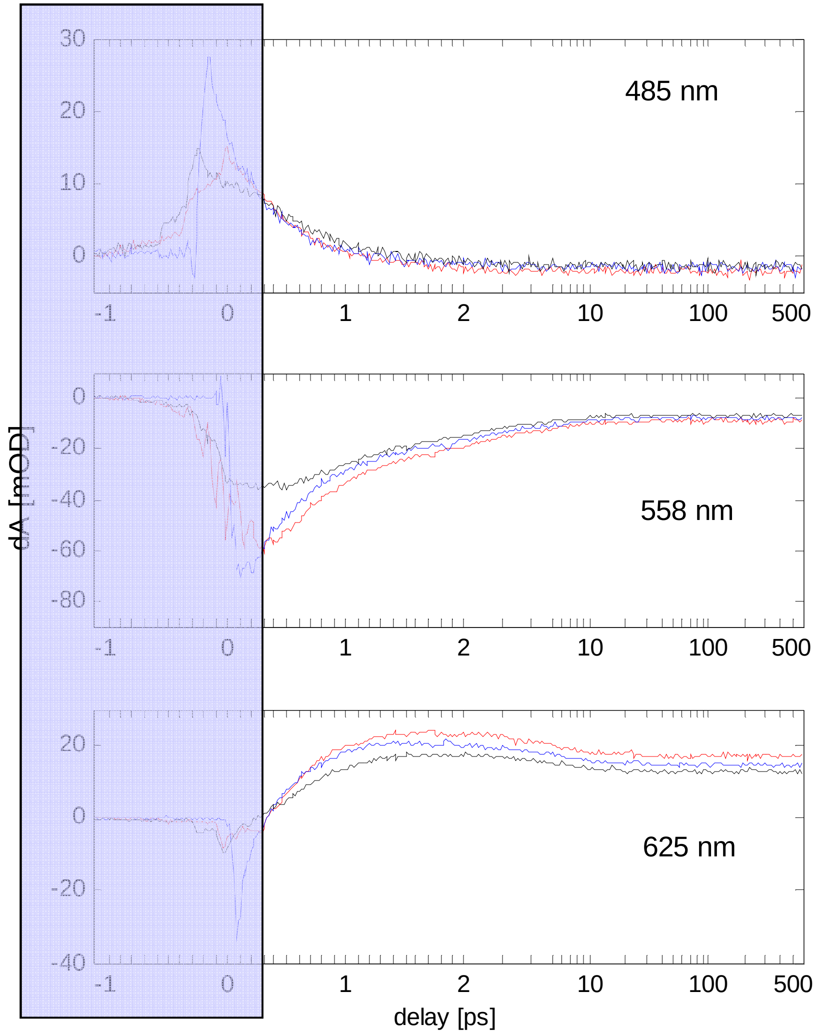
Phase dependence of the reaction branching ratio should be reflected in the reaction dynamics

Pulse Shape Dependence of Molecular Dynamics



(A1,2) – without modulation; (B1,2) – with phase modulation; (C1,2) – with flipped phase modulation

• **Analysis of pump-probe kinetics driven by different pulses**

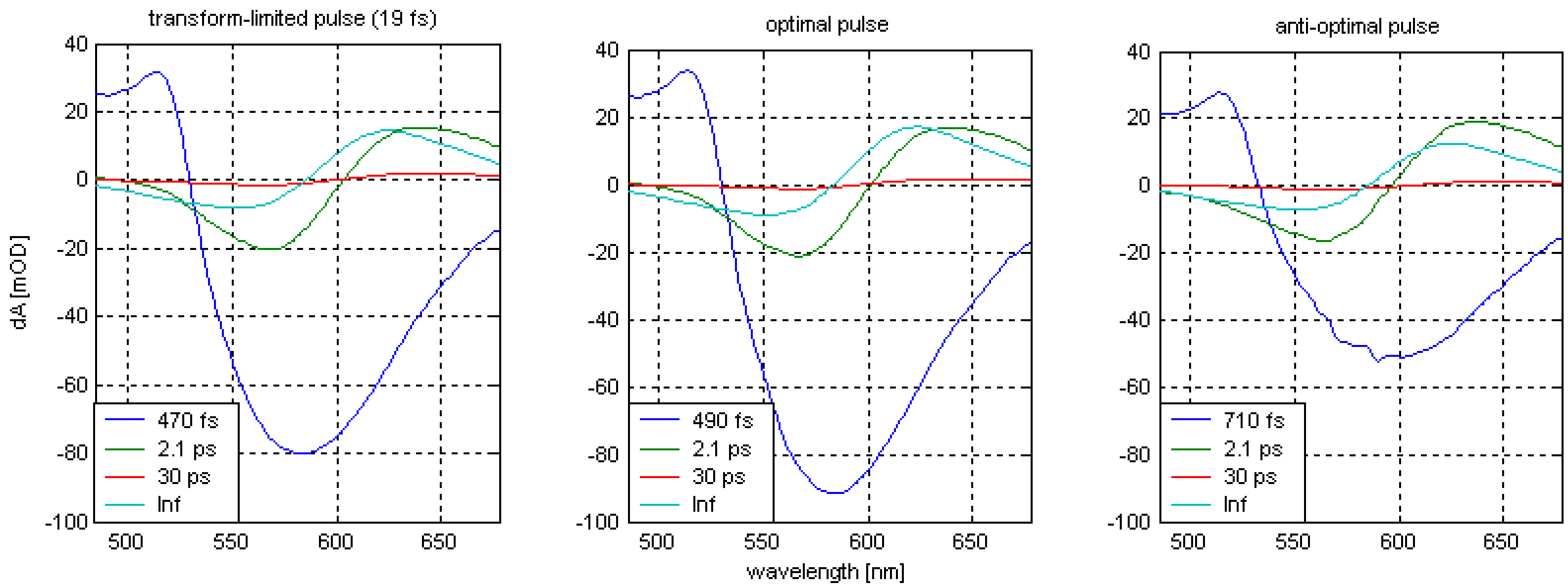


EXAMPLE:

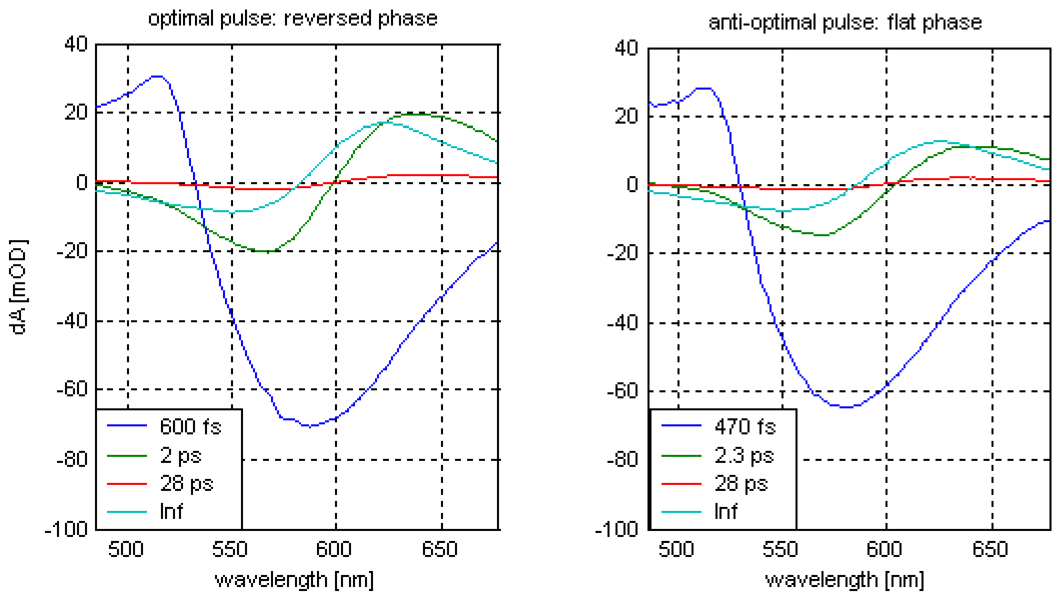
Several traces at different wavelengths
(note – actinic excitation energy all the same)

Blue – transform-limited
Red – optimal
Black – anti-optimal

• Global Spectral Analysis

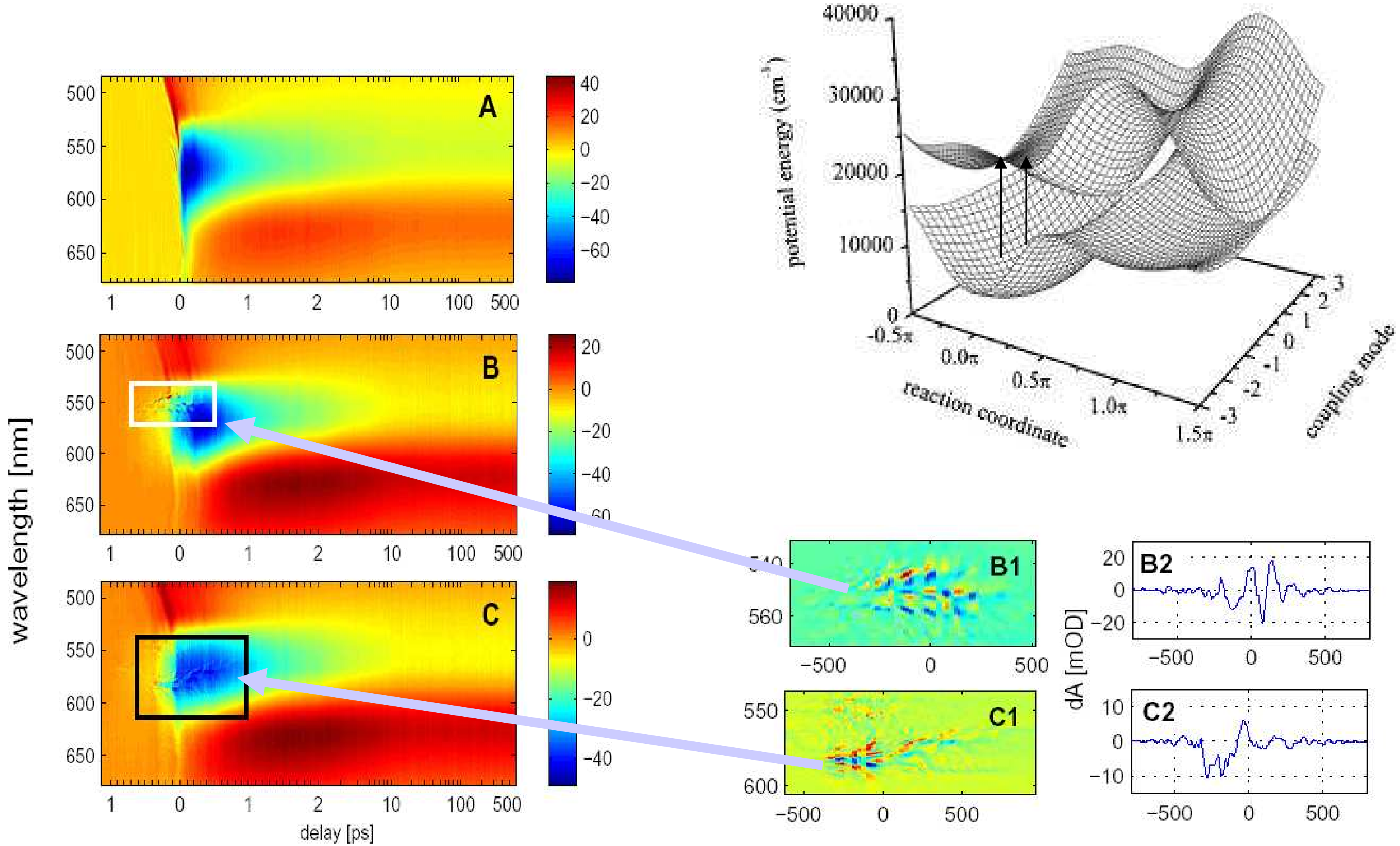


$$dA(t,\lambda) = IRF \otimes \sum_i A_i(\lambda) e^{-t/\tau_i}$$



Basics:
population / isomerization kinetics are ***sensitive*** to phase information contained in light

Coupling to Reaction Mode



⇒ Driving Large Amplitude Motion along Rxn Coordinate

Mechanism: Insight from Theoretical Studies

rhodopsin

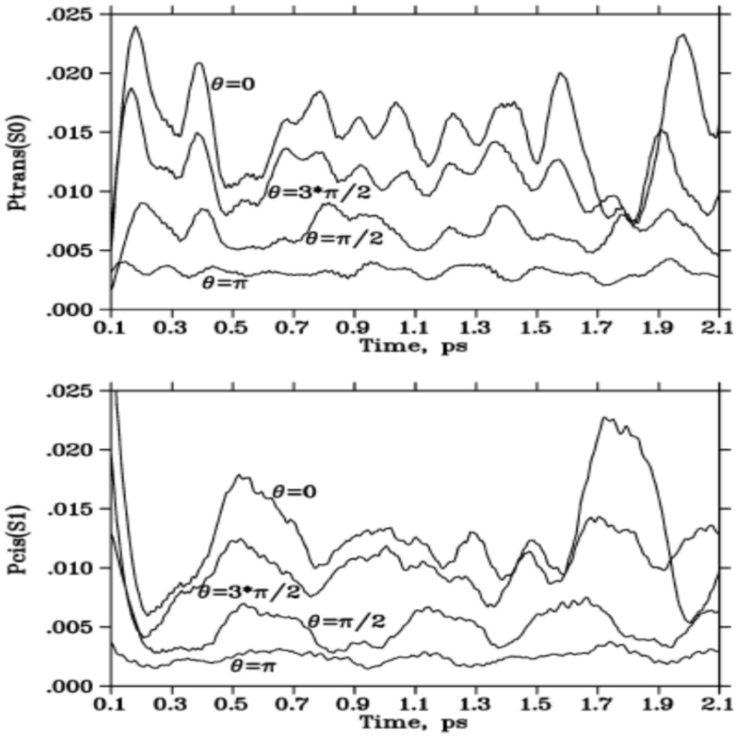


Figure 2. Time-dependent probability of the system to be in the trans configuration of the S_0 electronic state, $P_{trans}^{(S_0)}(t)$ (upper panel), and the cis configuration of the S_1 electronic state, $P_{cis}^{(S_1)}(t)$ (lower panel), for relative pump pulse phases $\theta = 0, 3\pi/2, \pi/2$, and π.

S. Flores, V. Baptista, JPCB, **2004**, 6745 ⇒ pulse shape comprised of 2 guassians

TDSCF: Full quantum treatment (25) modes with empirical coupling to protein

⇒Same excitation level as experiment: predicts 30% control

⇒Time dependent reaction probability: material response is time variant viz bifurcation point in Conical Intersection

CONCLUSIONS (CIRCA 2009)

- Trans-cis isomerization (branching ratio) of retinal molecule in bacteriorhodopsin **can be controlled** in weak field limit using tailored excitation pulses (40-50%)

$\Rightarrow$ **control of a biological function**

- *Fundamental differences for weak field control in closed and open quantum systems*

- Optimal pulse displays very regular temporal- and spectral structure $\Rightarrow$ coincides with driving torsional reaction mode modulating the conical intersection
  - central spectral components are modulated with period of ~ 150, 80, 45 fs

$\Rightarrow$ ***Coherence is conserved through barrier crossing events in biological systems — and can be controlled/manipulated. "Proteins know how to surf"***

EXTENTION TO STRONG FIELD: THE CHALLENGE

Control of retinal isomerization in bacteriorhodopsin in the high-intensity regime

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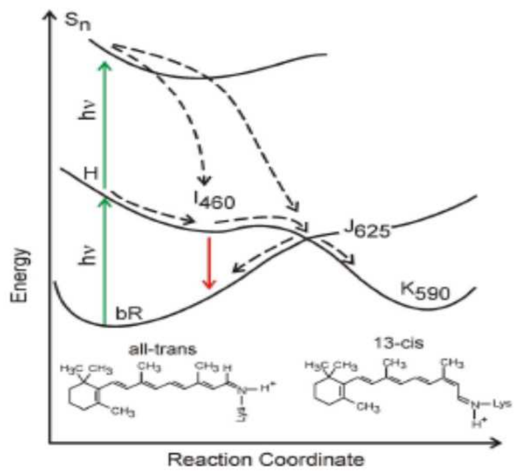
[a]Department of Physics, University of Michigan, Ann Arbor, MI 48109; [b]PULSE Institute and Department of Physics, Stanford University, Stanford, CA 94305; and [c]School of Medicine, University of California, Irvine, CA 92697

Contributed by Philip H. Bucksbaum, May 20, 2009 (sent for review October 13, 2008)

A learning algorithm was used to manipulate optical pulse shapes and optimize retinal isomerization in bacteriorhodopsin, for excitation levels up to 1.8 × 10^{16} photons per square centimeter. Below 1/3 the maximum excitation level, the yield was not sensitive to pulse shape. Above this level the learning algorithm found that a Fourier-transform-limited (TL) pulse maximized the 13-cis population. For this optimal pulse the yield increases linearly with intensity well beyond the saturation of the first excited state. To understand these results we performed systematic searches varying the chirp and energy of the pump pulses while monitoring the isomerization yield. The results are interpreted including the influence of 1-photon and multiphoton transitions. The population dynamics in each intermediate conformation and the final branching ratio between the all-trans and 13-cis isomers are modified by changes in the pulse energy and duration.

coherent control | photoisomerization | ultrafast science

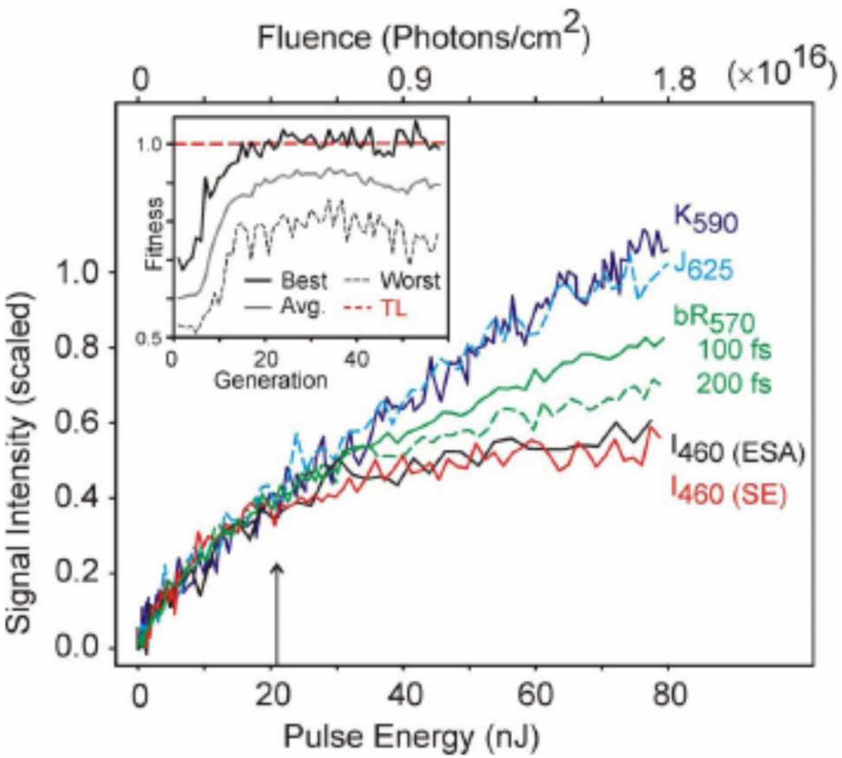


Coherent Control Absent in High Intensity Regime in contrast to all other systems ⇒ something different about biological systems >>>> COMPLEXITY<<<<<<<<<<<<

Isomerization is more efficient from higher lying electronic states.

⇒ How can an upper level state, never accessed, be more efficient than evolutionary optimized state?…….contradicts weak field control results

No Coherence in Control



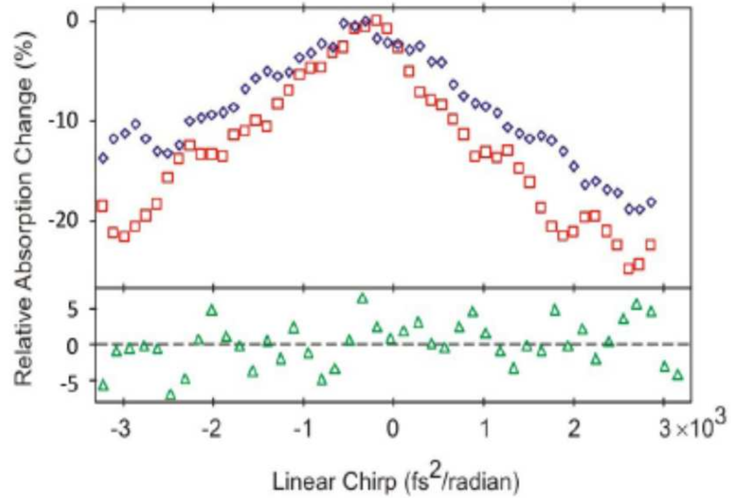


Fig. 4. Probe absorption change vs. chirp of the pump pulse. (*Upper*) The J_{625} (blue diamonds) and K_{590} (red squares) signals versus linear chirp at 80 nJ pulse energy. (*Lower*) K_{590} signal versus linear chirp at 12 nJ pulse energy (green triangles). All signals are measured at 650 nm. The J_{625} signal is measured at 2 ps and the K_{590} signal is measured at 40 ps.

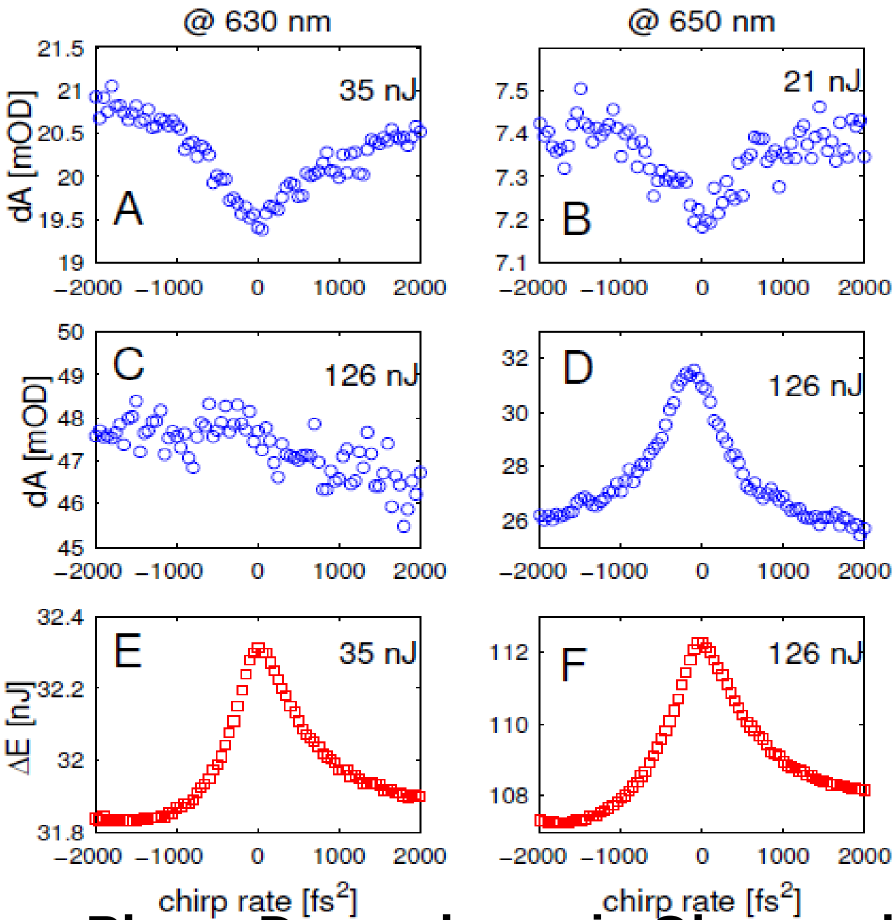
⇒

⇒Cis Formation Probed at 650 nm

Optimal Control Pulse is observed to be Transform Limited ⇒ No relative phase dependence, “control” only depends on peak power

Contradicts Weak Field Control Studies and generalized observation of increased control in strong fields

Experiment Repeated: Chirp scans



← **dA vs. chirp**

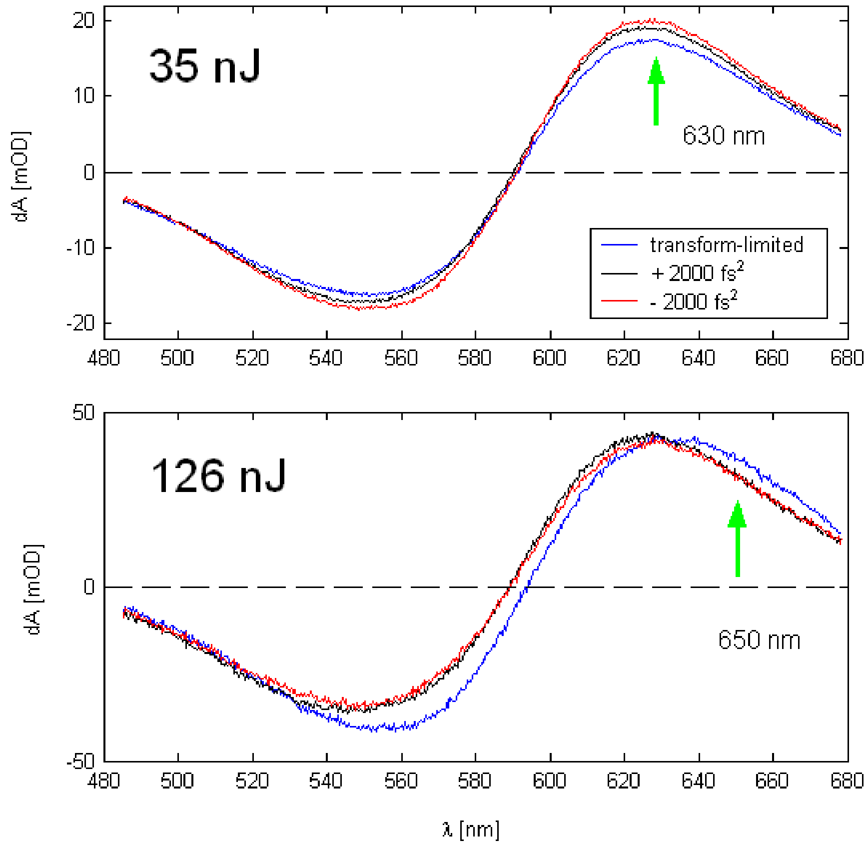
← **absorbed energy vs. chirp**

⇒ Phase Dependence is Observed and is Significant (16%)

⇒ Reproduced Results at Highest Intensity/Conditional Proof

⇒ Insufficient Sensitivity/wrong monitoring wavelength/not normalized to absorbed energy… rxn yield was not the observable

Differential absorption spectra measured at 40 ps delay after excitation (sample OD ~ 1)

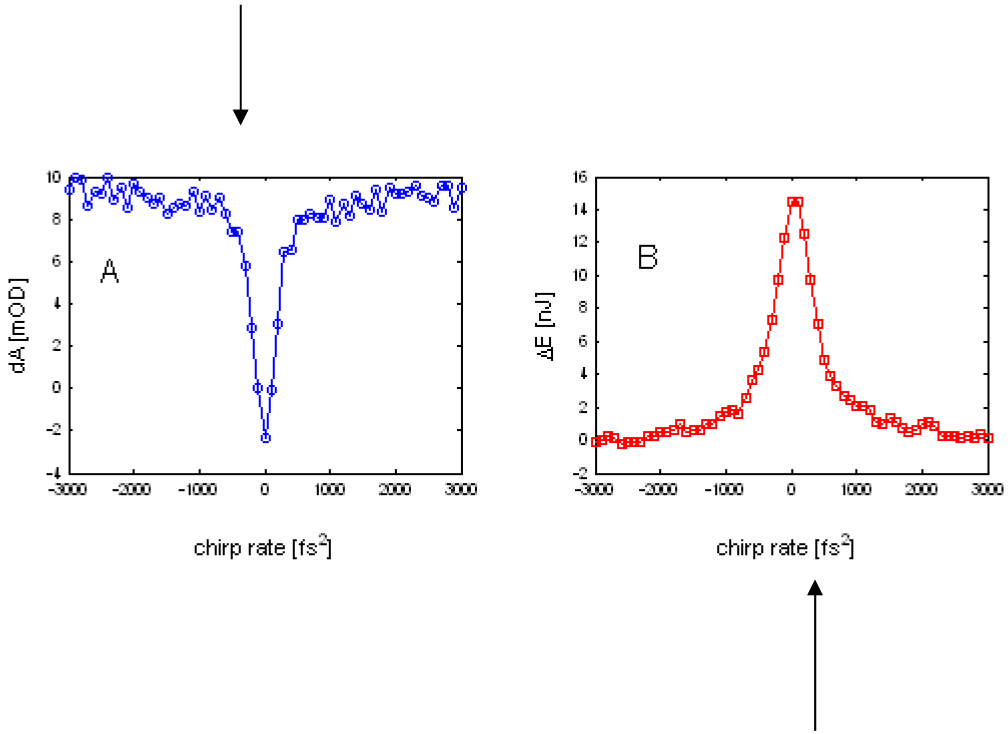


Origin of observed spectral shift
⇒ionization of bR and generation of solvated electrons

⇒ More than one photoproduct

CONTROL STUDY — BUFFER ONLY

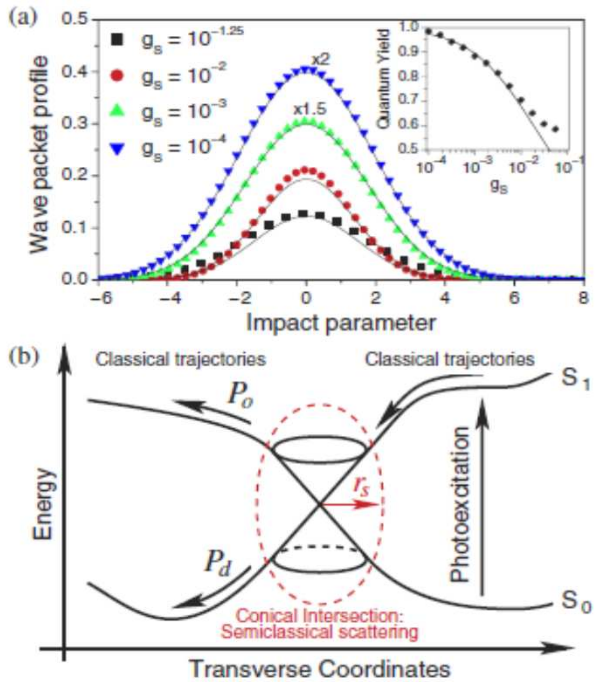
Chirp scan of very diluted sample (OD 0.2) measured @600 nm



Absorbed energy in pure buffer vs. chirp rate

Reproduces effect without protein → 10% of excitation absorbed due to multiphoton absorption/ionization under NONRESONANT CONDITIONS >>>> Orders of Magnitude larger for RESONANT CONDITIONS of bR

1) Intrinsic isomerization control: wave packet acceleration



Parameter g = $v^{-3/2}$

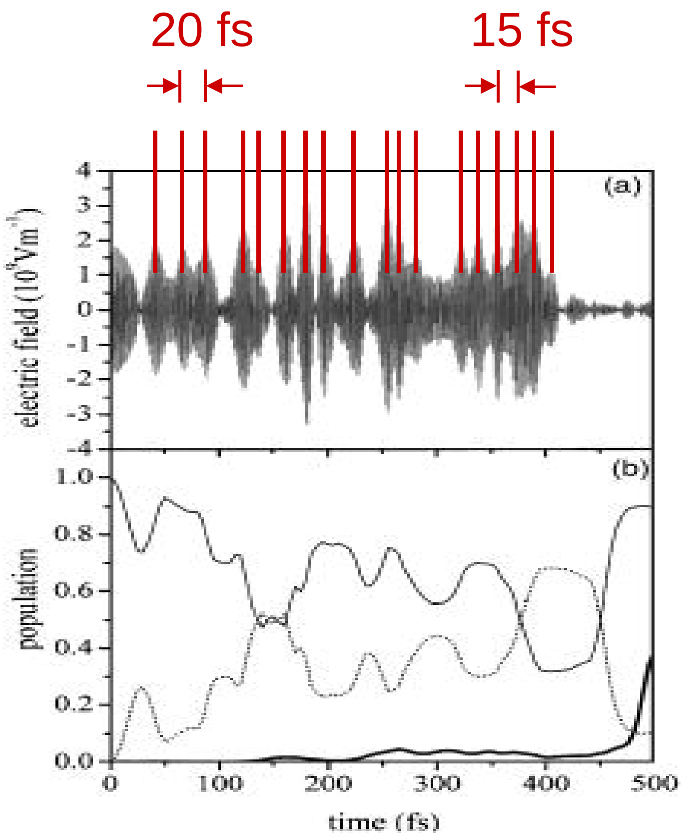
V – speed of wave packet going though the conical intersection "aperture" (i.e., chirp of pulse)

Negatively-chirped pulses should increases isomerization efficiency

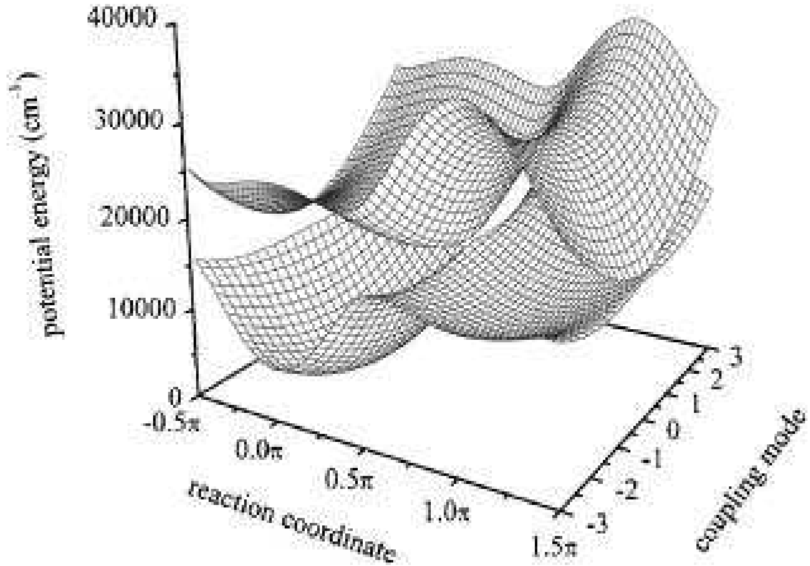
Piryatinski et al., *PRL* 223001 (2005)

Negative chirp enhances motion to conical intersection…less time for scattering into unreactive modes

2) Control of Isomerization: High Intensity Regime ("Exact")



Abe et al., J.Chem.Phys. 123, 144508 (2005)



• subpulses have a period of ~ 20 fs corresponding to a carbon backbone stretch of ~1600 cm^{-1}

Frozen two levels → does not include coupling to protein….15% for FC weighted wavepacket

General Feature ⇒ optimum pulse is composed of subpulses timed to modes involved in reaction

CONCLUSIONS (CIRCA 2010)

Coherent Control demonstrated from weak field to strong field limits

⇒***Fundamental differences for weak field control in closed and open quantum systems***

⇒**Key Message: Protein Structure Reduces the Reaction Coordinate to a Few Labile Coordinates**

⇒ **Coherent Control must be extended to Weak Field Limit to avoid multiphoton ionization/multiple reaction channels**

⇒ ***Coherence is conserved through barrier crossing events in biological systems — and can be controlled/manipulated. "Proteins know how to surf"***

Nagging Question: How to rationalize degree of Coherent Control with 10 fs regime Quantum Decoherence of the Optically Induced Polarization?

[redacted]

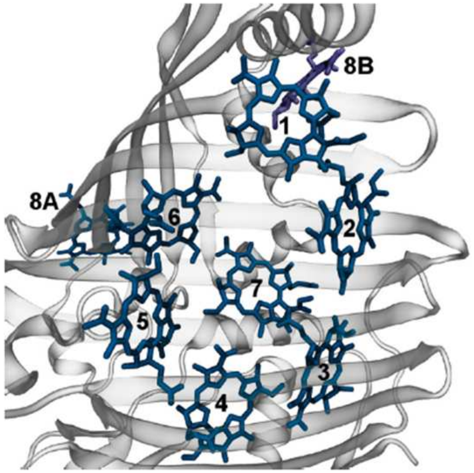
Characterizing Quantum Coherence in Biological Systems ⇒ Coherent Multidimensional Spectroscopy

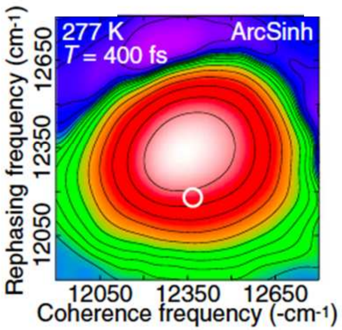
Motivation:

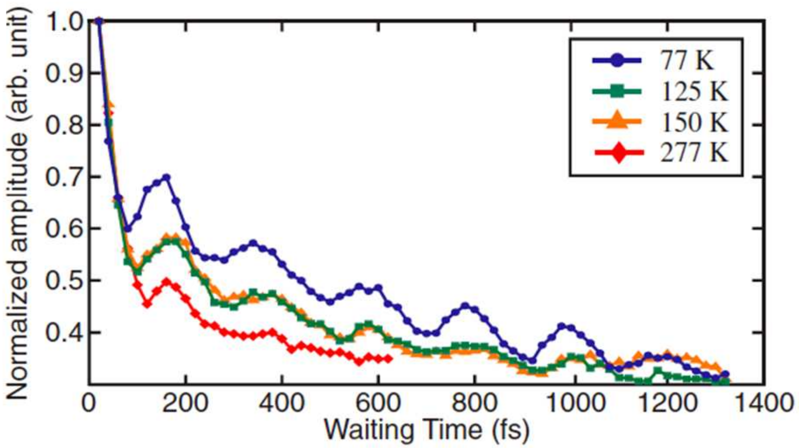
⇒Two-dimensional photon-echo electronic spectroscopy (2DPE) directly measures the homogeneous linewidth (pure dephasing, T2 contribution), couplings between states, and enables watching the state preparation evolve spectrally…more information on bR problem.

⇒ Anomolously long lived coherences have also been suggested to play a role in energy transport in photosynthetic systems…quantum or wave like transport…special role of the protein environment

Panitchayangkoon et al. , PNAS, 2010







Oberling, Strumpfer, Schulten, JPC, 2010

Understanding 2D-PE spectra

1) Ensemble of identical molecules

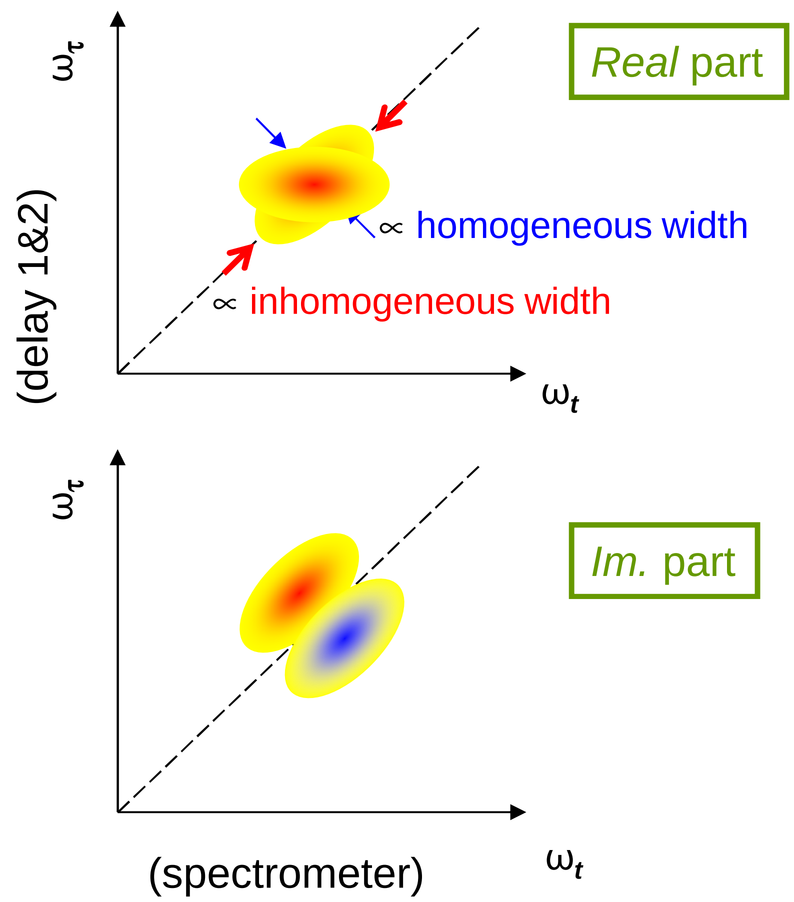
T = 0 (“correlation spectrum”)

$$S_{PE}(\omega_t,\omega_\tau) \propto \int_0^\infty dt\, e^{-2\mathrm{Re}(g(t))} e^{i\omega_t t} \int_0^\infty d\tau\, \chi(t-\tau) e^{-2g^*(\tau)} e^{g^*(t+\tau)} e^{i\omega_\tau \tau}$$

correlations

→ link between ω_τ, ω_t

Increasing T → ∞



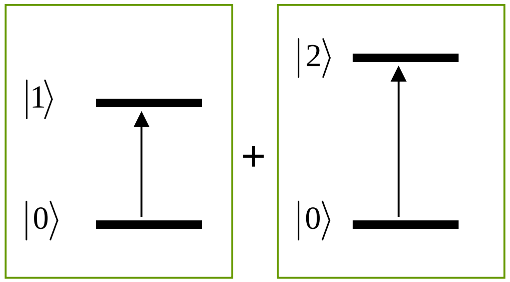
T → ∞ (no inhomogeneous broadening)

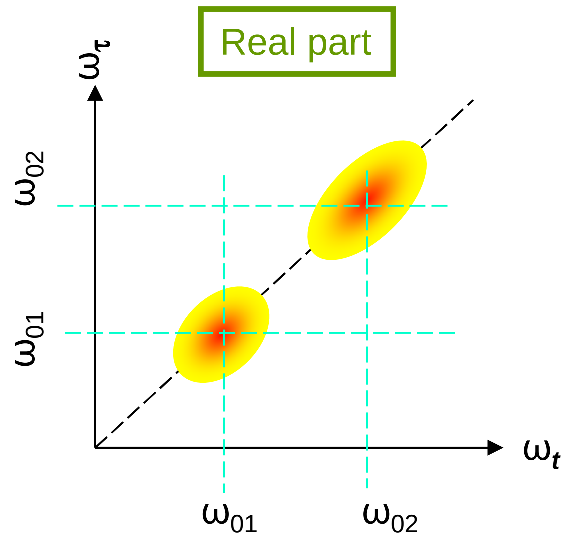
$$S_{PE}(\omega_t,\omega_\tau) \propto \sigma_a(\omega_\tau)\{\sigma_a(\omega_t)+\sigma_f(\omega_t)+iKK[\sigma_a(\omega_t)+\sigma_f(\omega_t)]\}$$

→ there is no link between variables!

2) Uncoupled molecules with different electronic transitions

Level diagram:

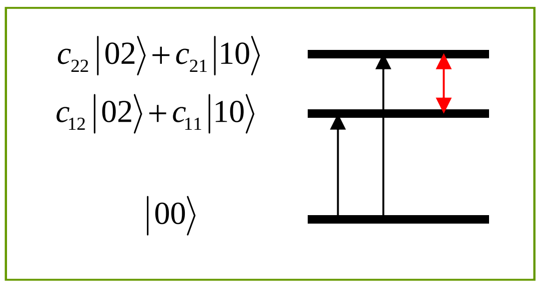




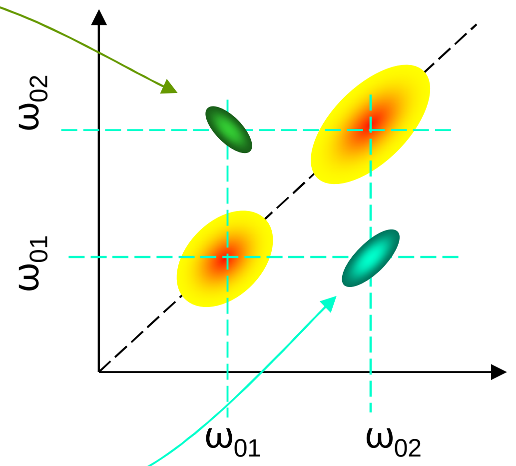
Density matrix (2 molecules):

$$\rho(t) = \begin{Bmatrix} \rho_{22} & 0 & \rho_{20}\cos(\omega_{20}t) \\ 0 & \rho_{11} & \rho_{10}\cos(\omega_{10}t) \\ \rho_{02}\sin(\omega_{20}t) & \rho_{01}\sin(\omega_{10}t) & \rho_{00} \end{Bmatrix}$$

3) Excitonically-coupled molecules (molecular aggregate)

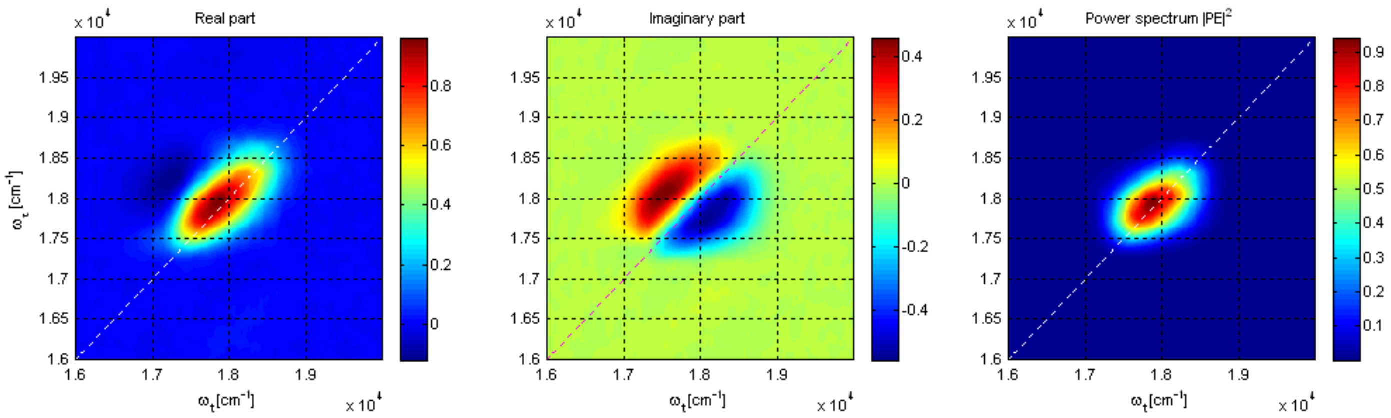


$$\rho(t) = \begin{Bmatrix} \rho_{22} & \rho_{21}\cos(\omega_{21}t) & \rho_{20}\cos(\omega_{20}t) \\ \rho_{12}\sin(\omega_{12}t) & \rho_{11} & \rho_{10}\cos(\omega_{10}t) \\ \rho_{02}\sin(\omega_{20}t) & \rho_{01}\sin(\omega_{10}t) & \rho_{00} \end{Bmatrix}$$

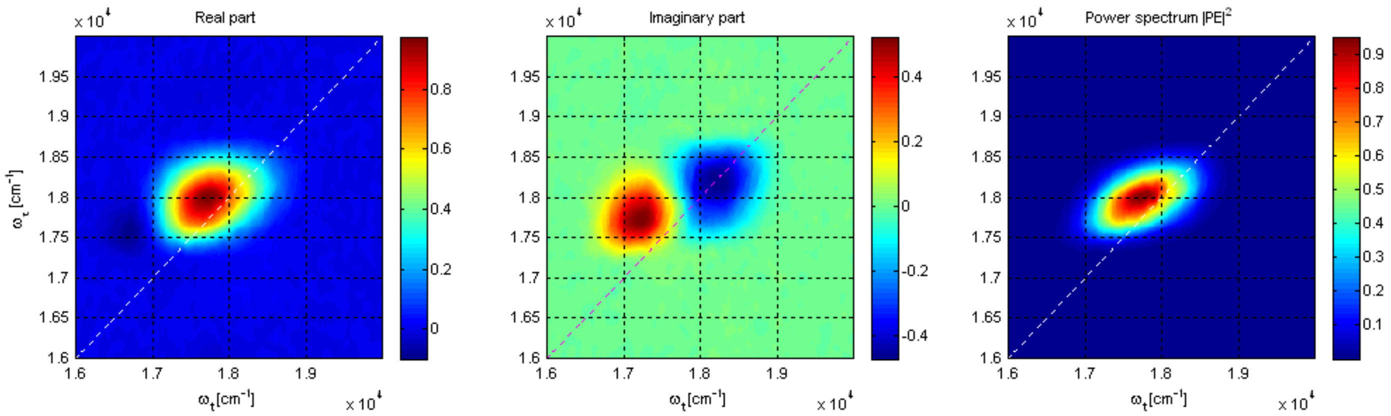


Example “TLS”: Rhodamine 101

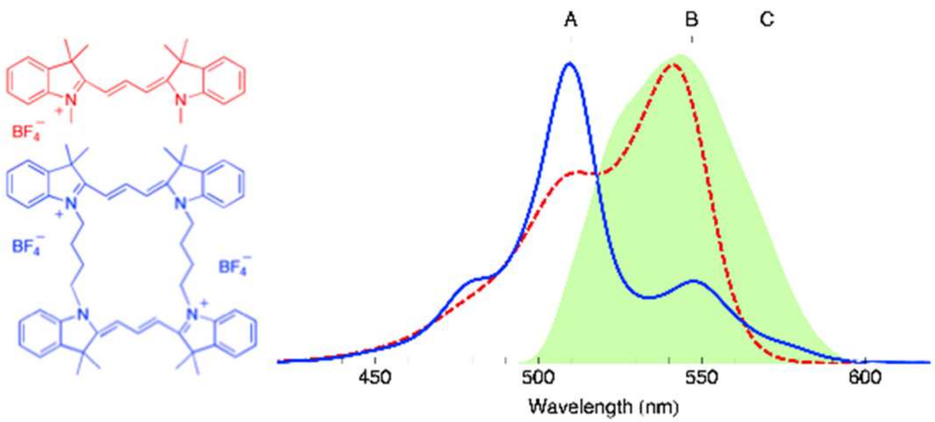
T = 0 fs



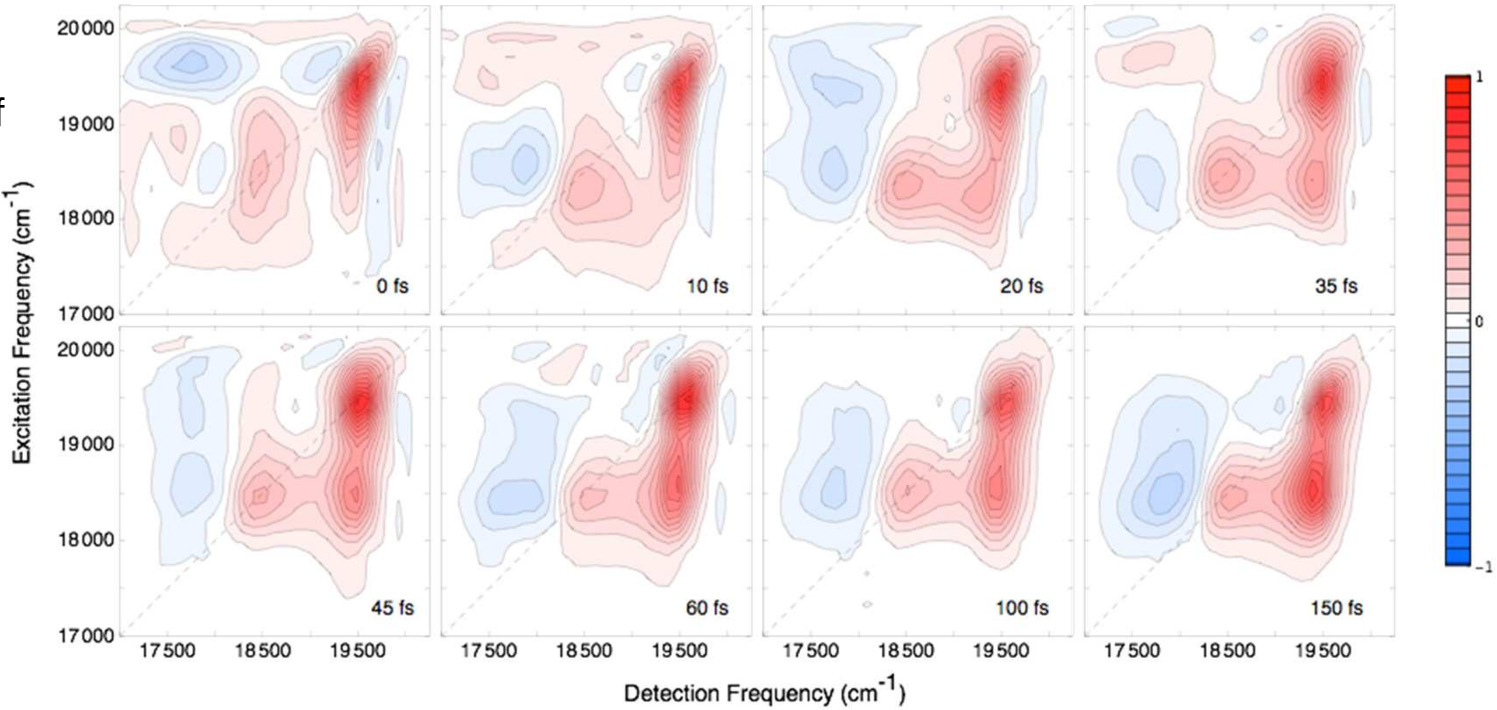
T = 40 ps



Model Dimer:

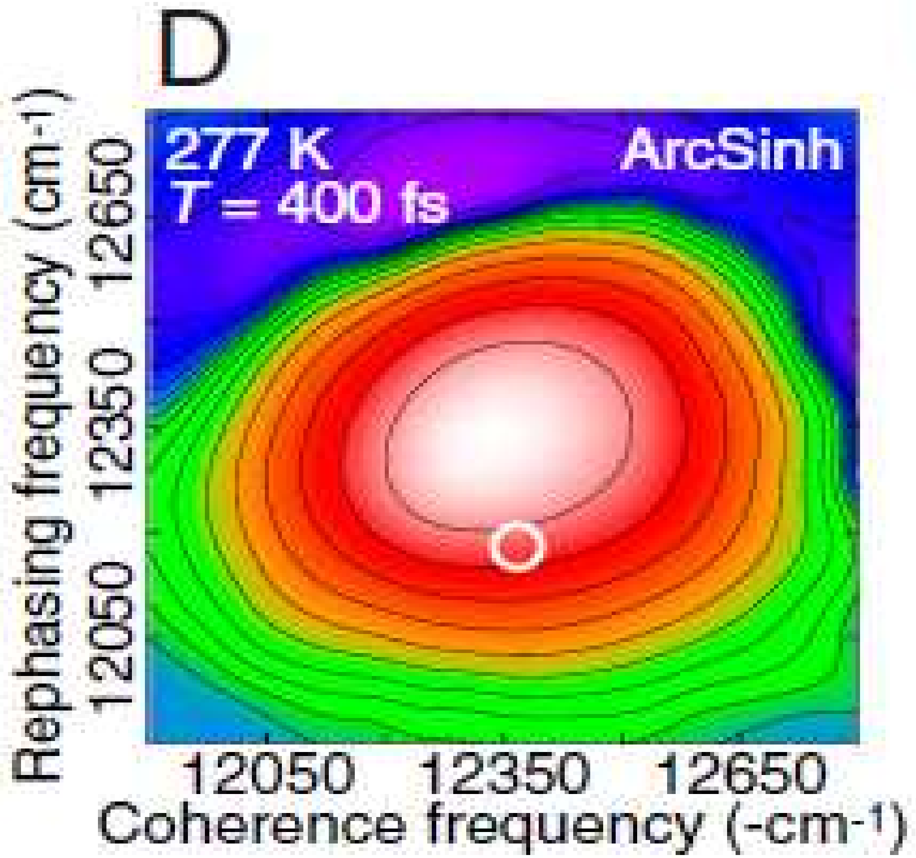


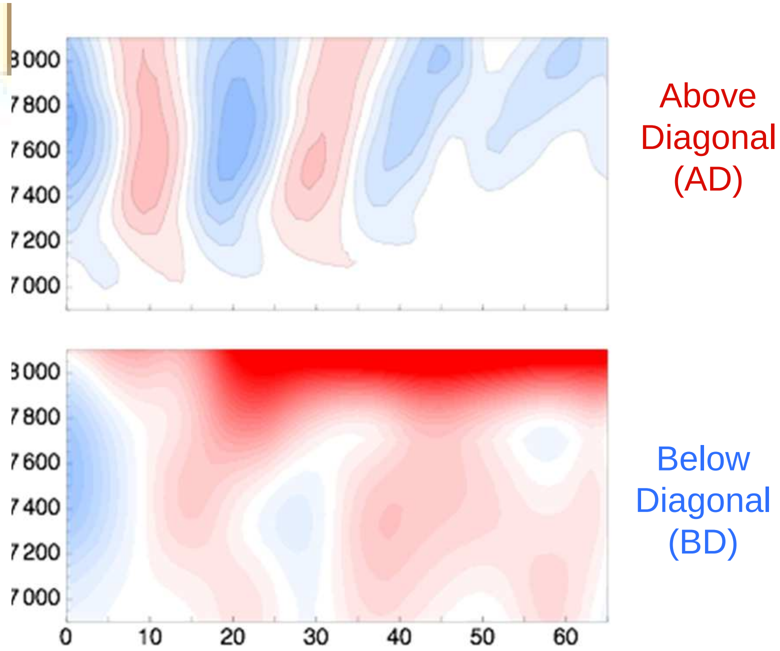
Real part of total 2D Spectra for selected T



- Clearly resolved cross peaks – note amplitude is as expected from cross terms (e.g. $\mu^2_A\mu^2_C$)

Quantum Beats/Homogeneous Lifetime

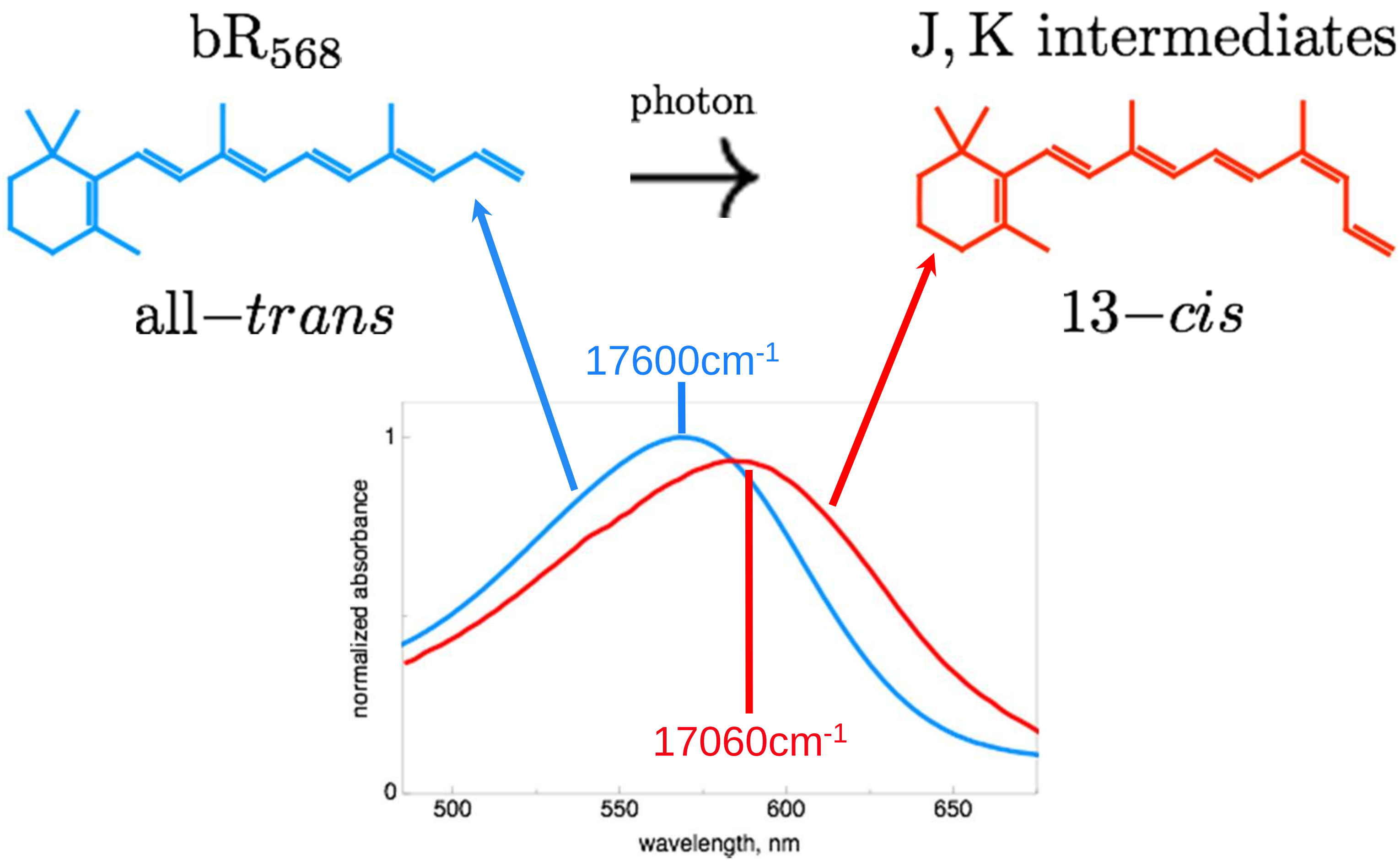




	AD	BD
ω(cm^{-1})	1501	1550
τ (fs)	41.7	49.2

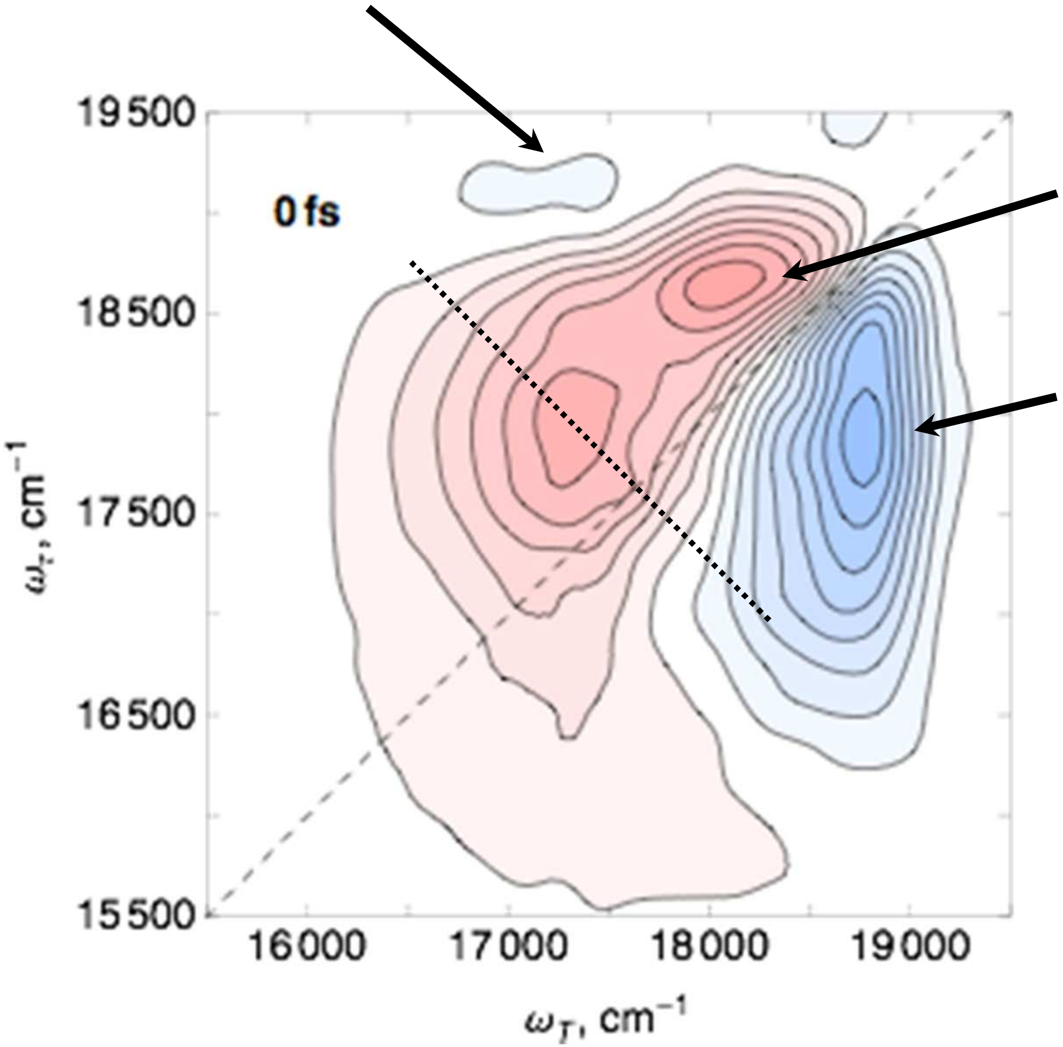
⇒ The antidiagonal line width and off diagonal components are causally related (FT)…long lived quantum beats are vibrational (Jonas et al – vibrational coherences enhance ET)

Bacteriorhodopsin



T = 0 fs

negative feature growing
in near cis max



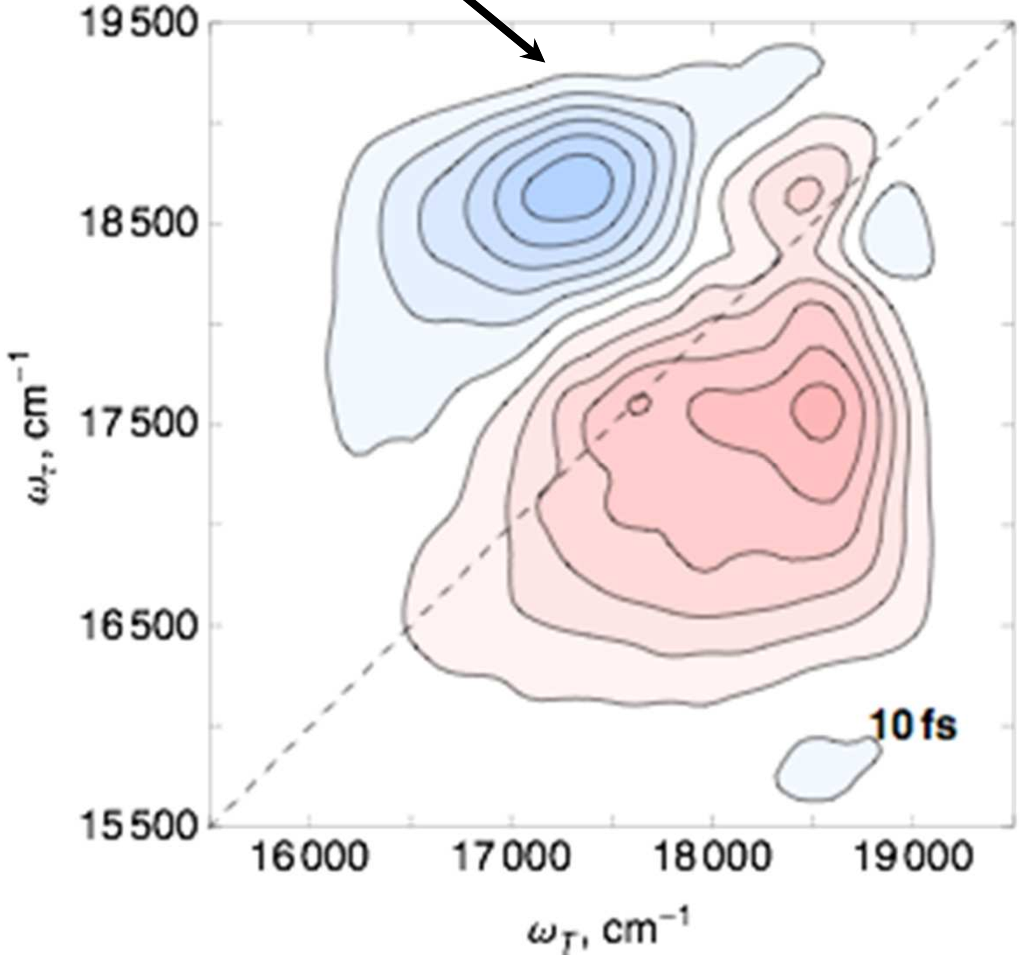
- clear vibronic structure at HOOP frequency

- negative Kerr effect

- anti-diagonal linewidth: 936 cm^{-1}, results in a dephasing time of 11 fs (upper bound)

T = 10 fs

negative feature not due to ESA



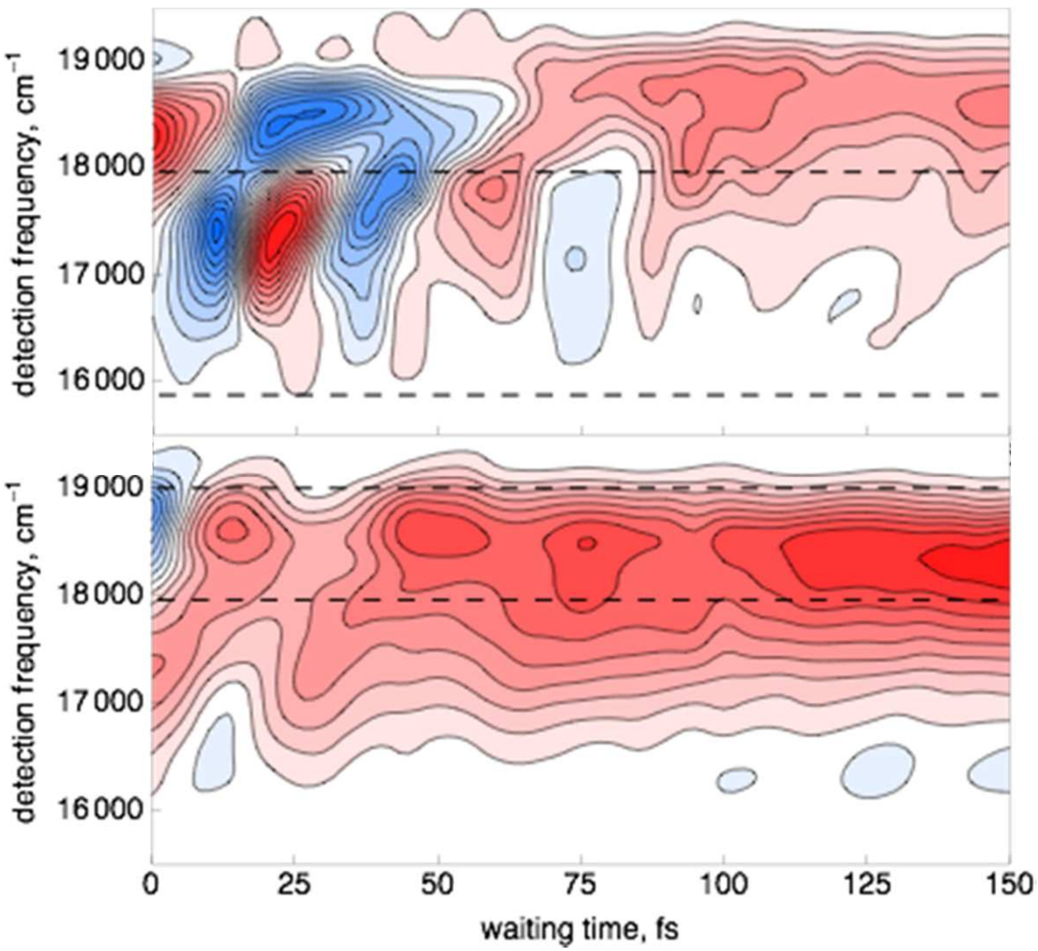
- negative feature grows
- located (spectrally) at the cis absorption max!
- correlated with vibronic bleach feature

- vibronic band shows off-diagonal coupling

Temporal dynamics

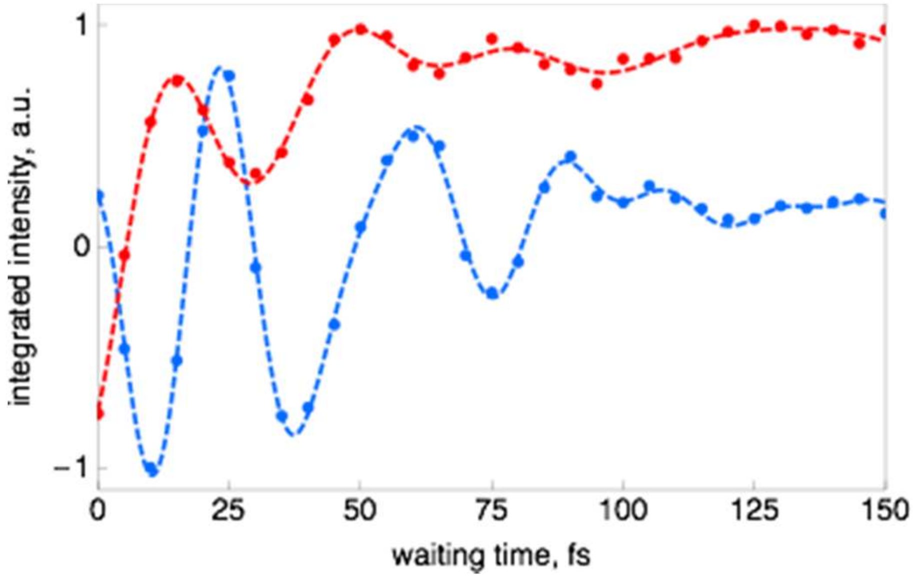
Effect of pumping about the vibrational shoulder at 18500cm^{-1}: clear oscillatory dynamics of the cis-like feature

Effect of pumping the linear absorption maximum at 17500cm^{-1}: vibrational cross-peak



Fit results

$$\sum_{i=1}^{4} A_i e^{-t/a_i} \sin\left(\frac{2\pi t}{b_i} + c_i\right) + d$$



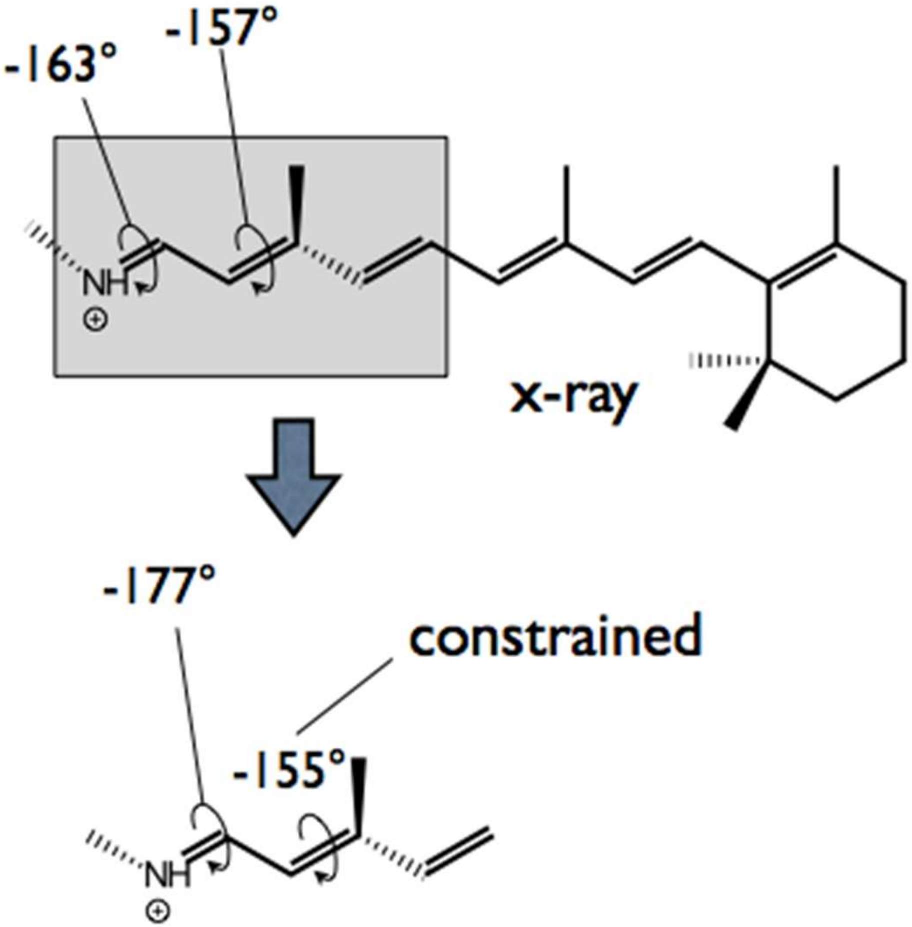
Frequency, cm^{-1}	Phase, rad	Amplitude, a.u.	Decay, fs	Mode
823	1.87	0.838	54	HOOP
210	2.73	0.731	40	Torsion
1560	1.09	0.453	53	C=C stretch
1106	2.20	0.935	42	C-C stretch
986	1.95	0.772	29	HOOP

⇒ **Very strong coupling between trans and cis electronic surfaces by the very modes directing the reaction coordinate**

⇒ **HIGHLY DIRECTED**

QM/MM calculations

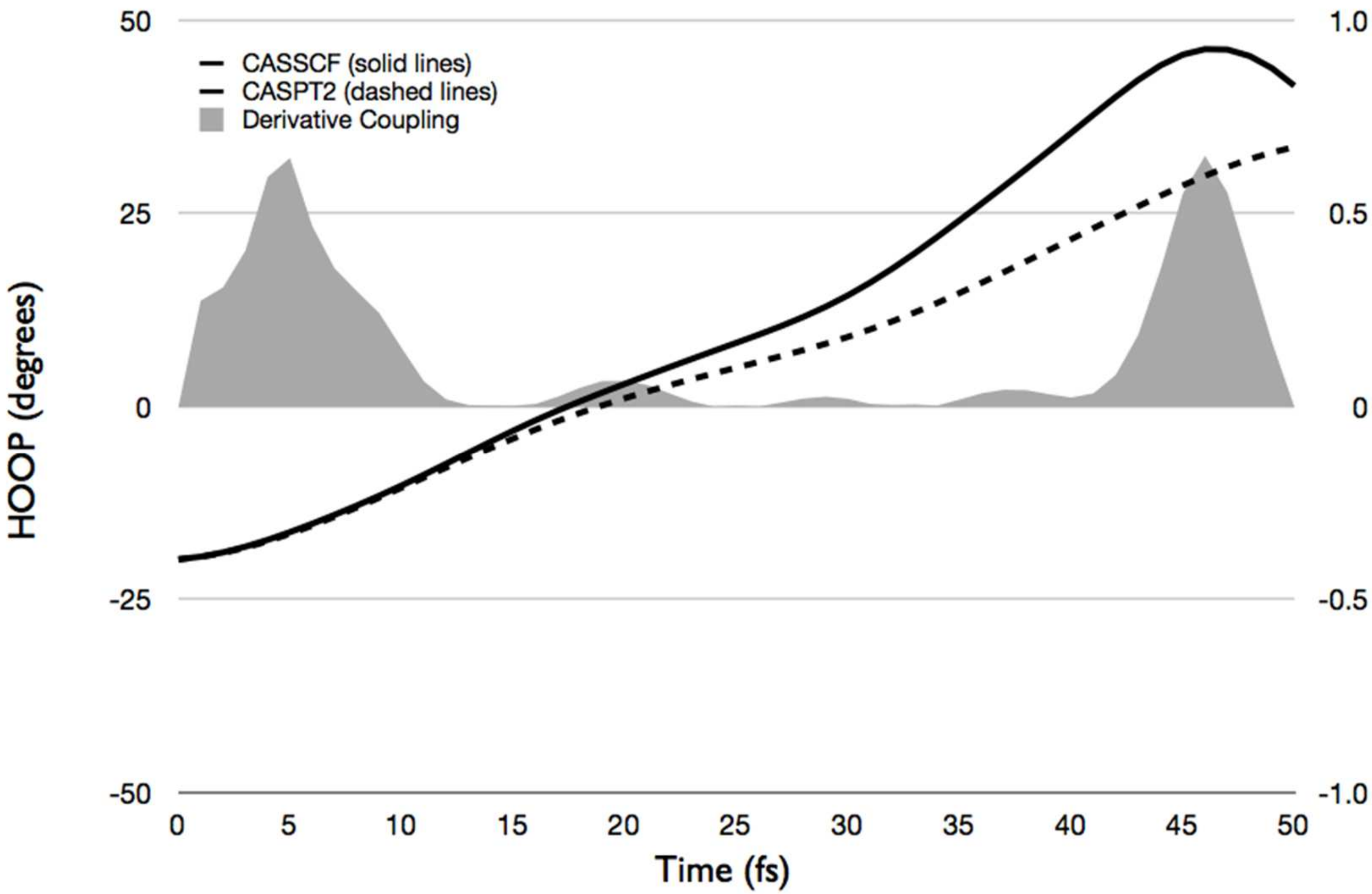
(collaborators: Massimo Olivucci and Samer Gozem)



bR retinal chromophore

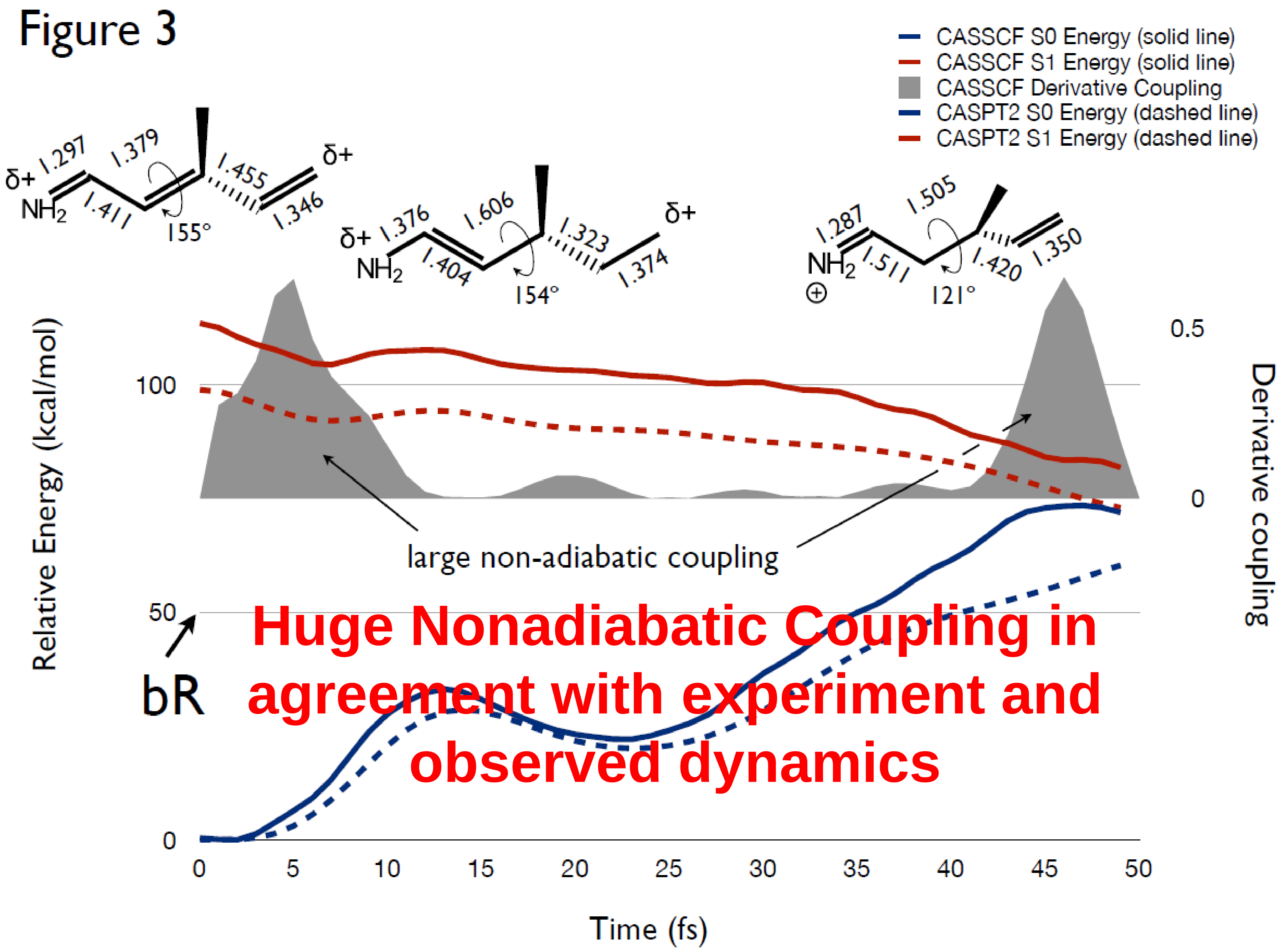
minimal model

HOOP mode dynamics



smoothly varying over initial time period

Energy and Derivative Coupling along the FC Trajectory



Huge Nonadiabatic Coupling in agreement with experiment and observed dynamics

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⇒ ***Coherence is conserved through barrier crossing events in biological systems — and can be controlled/manipulated. "Proteins know how to surf"***

Vibrational Coupling/Coherences exploited for optimizing reaction coordinates/functions in biological systems