Quantum Coherence & Dynamics in Biological Processes: Molecular Isomerization in Vision

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The issue --

Background – (at least since Schrodinger, 1944):

1. Molecular behavior underlies biological function

2. Quantum mechanics are the rules of molecular behavior

3. Hence, Interest in e.g. "nontrivial" quantum effects

Key question: Are such features manifest in nature?

[See, e.g., interesting debate --
"Quantum Aspects of Life", Imperial College Press, 2008]

Why not? Decoherence ← → effect of the environment
→ destroys quantum effects

Significant place to look in Biology: Light-Induced Processes

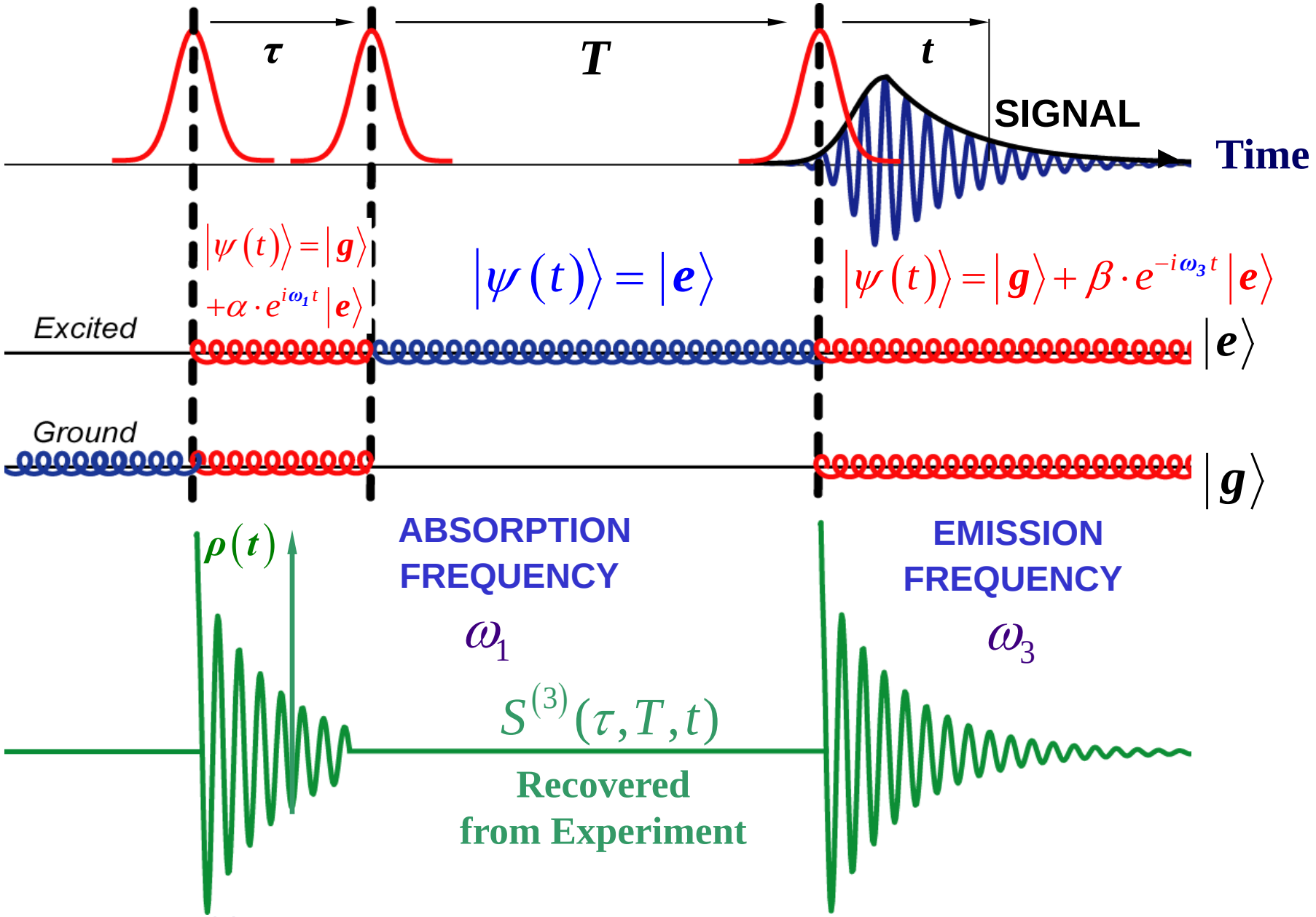
Fundamental Systems: (Vision, Photosynthesis, etc.)

(Indeed an AFOSR-funding transition period)

Input aided by modern laser based experiments

in pulsed laser experiments ---
oscillatory signals = “coherences” = termed quantum effects

Observations from, e.g., 2D Spectroscopy (Fleming/Engel/Scholes/Miller/Ogilvie)



- Obtain $S^{(3)}(w_1, T, w_3)$ by double Fourier Transformations in τ and t
- Retrieves Correlation between Absorption and Emission Frequencies

W.r.t. coherences, experiments show, in paradigmatic systems

E.g. , Photosynthetic Light Harvesting Systems

by 2D photon echo

Observation in FMO, PC645: longer-than-expected, then presumed, electronic coherence (> 500 fs, where 10 fs expected)

E.g. Visual Process

Rhodopsin-type Isomerization by pump probe, more recent fs multidimensional spectroscopy;

Observation: coherent oscillatory dynamics

Enthusiasm in the latter case, for example ---

Enthusiasm for dynamics of retinal in vision --- one sees quantum coherent dynamics within an apparently very hostile (decohering) environment.

E.g.

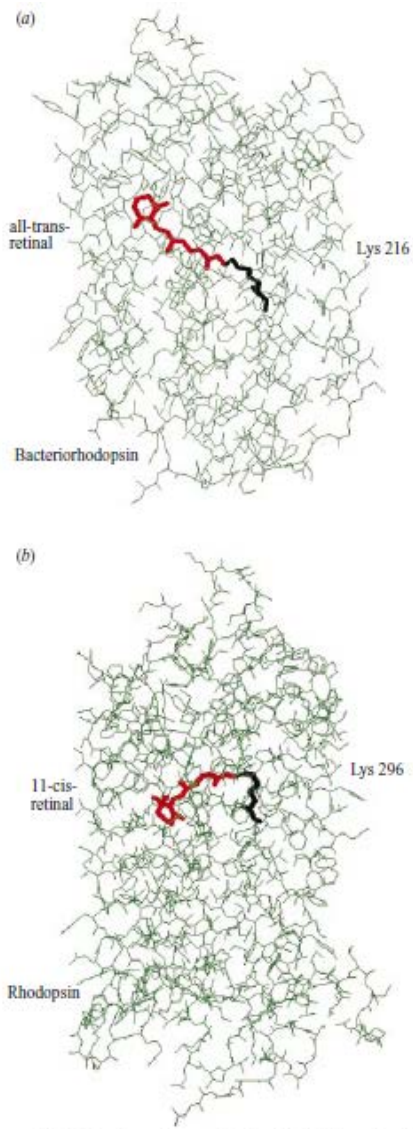


Fig. 14. Crystal structures of bR (*a*) and vertebrate rhodopsin (*b*). The retinyl groups are shown in red, and the lysine residues to which they are attached in black. The rhodopsin coordinates are from Palczewski *et al.* (2000); the bR coordinates, from Luecke *et al.* (1999b). The proteins are shown in roughly similar orientations, with the 7-transmembrane α-helices of each protein running vertically, the N-terminus at the top, and the first transmembrane α-helix from this terminus on the right.

Thus we have:

1. Highly unexpected timescales observed for the flow of electronic energy in some light induced dynamics (2 ps); long-lived coherent dynamics of molecules in visionary process (control seen over 20 ps).

2. Unexpected because system is both nanoscale system with strong decoherence expected (10 fs for electronic).

Significant biologically?

One punch line: To show you that:

Experimental light-induced coherences are not observed in nature.

Often stated ultrafast rates are not the rates in nature.

But are significant stationary quantum (?) coherences due to system-environment interactions.

First what are we looking for?

“Non-trivial quantum effects”

Some Definitions --

"Nontrivial Quantum" – Displaying features like interference, entanglement, nonlocality. Tests: e.g., Bell Inequalities, Leggett-Garg measurement based tests, delayed choice, quantum erasure, etc. [Intro – see Scholak and Brumer, Adv. Chem. Phys 162, 39 (2017)]

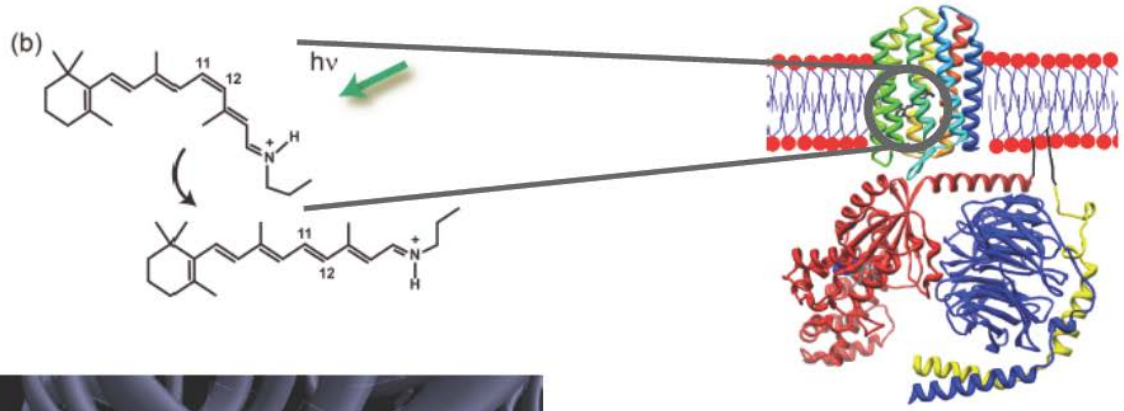
Status in "Nature" **--- Never tested;**
Arguments "for" are reliant on pulsed-laser-induced oscillations—coherence related.

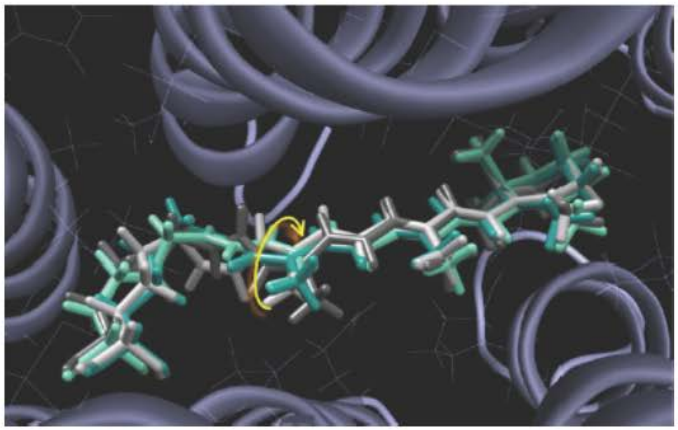
"Coherences" - Couplings between energy eigenstates of the Hamiltonians; Relevant-- (i) Light-induced time dependent (oscillatory), (ii) Light-induced time (in)dependent (Fano), (iii) Induced by system-bath couplings (time independent); Here, not delocalization.

What is done expt'ly?

Our system here

Visual excitation: Main facts





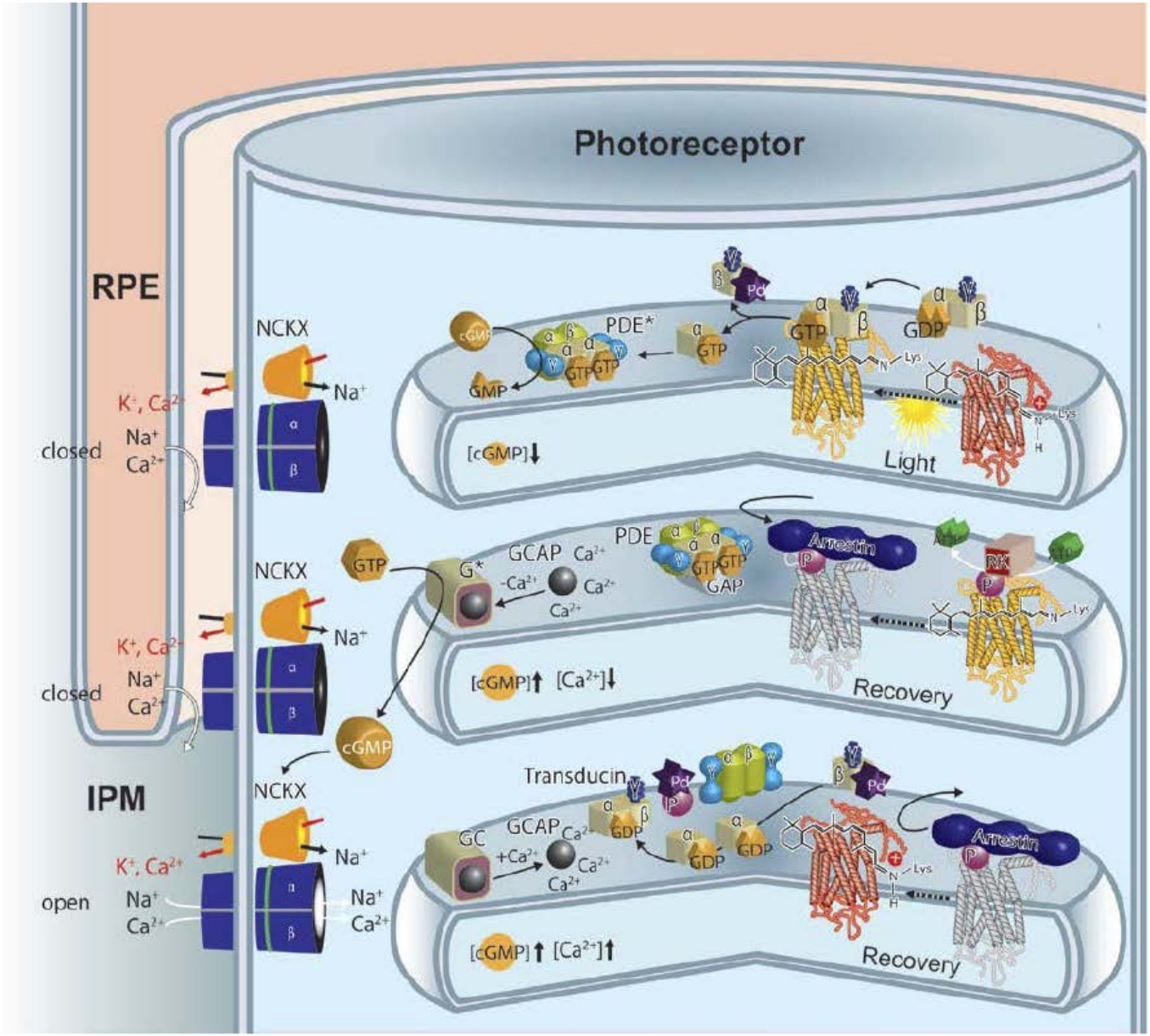
Rhodopsin

Sensory rhodopsin II (rainbow colored) embedded in a lipid bilayer (heads red and tails blue) with Transducin (G_t) below it.

11*cis* → all-*trans* photoisomerization

First step in transduction

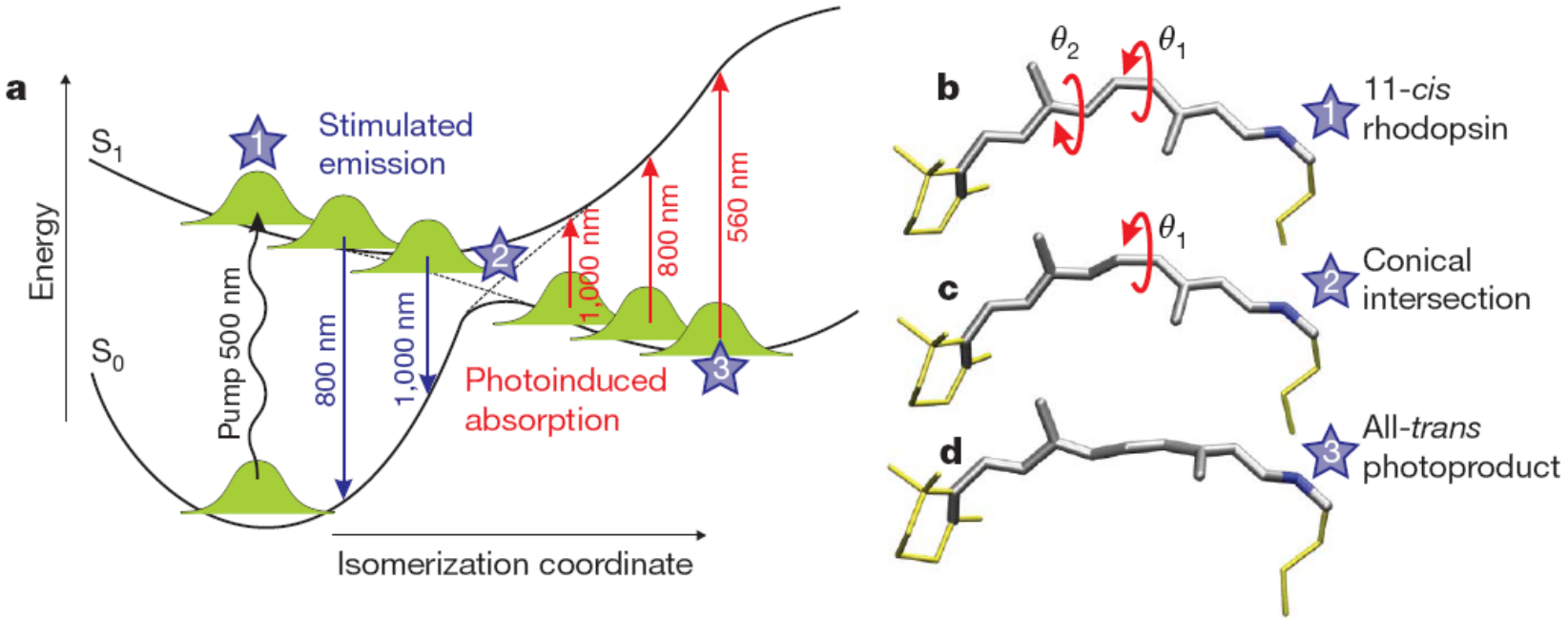
Citation: Palczewski K. Chemistry and biology of the initial steps in vision: the Friedenwald lecture. *Invest Ophthalmol Vis Sci*. 2014;55:6651–6672. DOI:10.1167/iovs.14-15502



Light absorbing step
Cis to trans

Regenerate cis

Where cis-trans photoisomerization is



Polli et al, Nature, 467, 440 (2010)

Coherent Laser Results: Long-standing

Central Seminal Observation– Vibrational Coherence in Pulsed Laser Excitation of Retinal, for approx. 550 fs Shank's group

Vibrationally Coherent Photochemistry in the Femtosecond Primary Event of Vision

Qing Wang, Robert W. Schoenlein, Linda A. Peteanu,*
Richard A. Mathies, Charles V. Shank

Science, 266, 422 (1994)

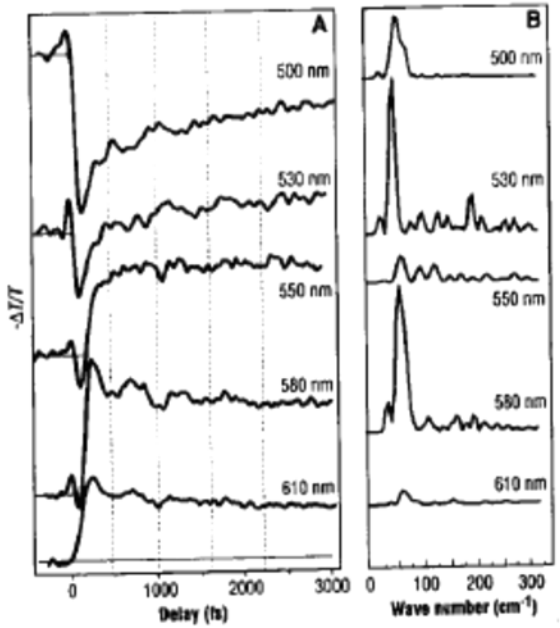


Fig. 3. (**A**) Differential transient absorption measurements probing a broad spectral range of the photoproduct absorption after excitation of rhodopsin with a 35-fs pump pulse at 500 nm. (**B**) Fourier transform analysis of the oscillations in the time-resolved data in (A). Before Fourier analysis, a smooth background consisting of a low-order polynomial fit was subtracted. The data at all wavelengths are transformed over the same time range of 200 to 3000 fs, with the lower limit constrained by the formation time of the photoproduct.

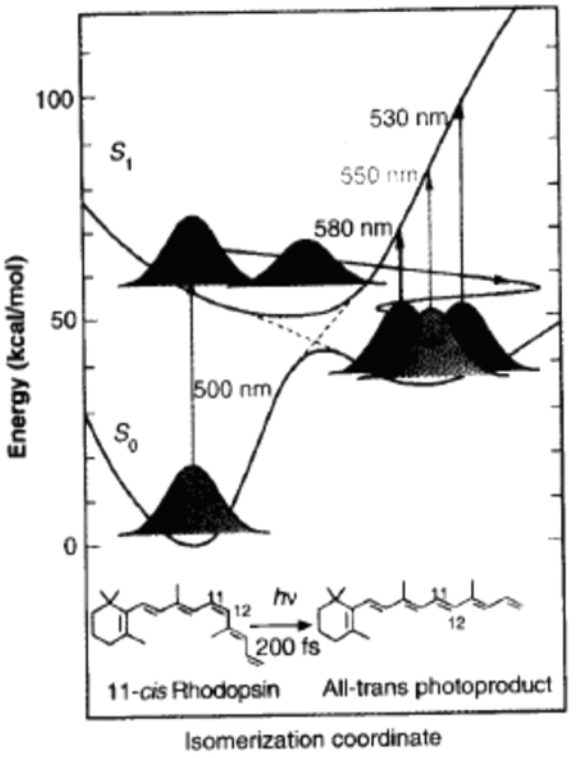


Fig. 1. Schematic potential energy surfaces for the femtosecond isomerization of rhodopsin after optical excitation of the molecule from the ground state S_0 to the excited state S_1. The wave packets in the photoproduct potential well illustrate how ground-state vibrational motion effects the photoproduct absorption. The dashed lines indicate the diabatic pathway along which the reaction proceeds.

There is much earlier work and, most recently, ---

ARTICLES
PUBLISHED ONLINE: 16 NOVEMBER 2015 | DOI: 10.1038/NCHEM.2398
nature chemistry

Local vibrational coherences drive the primary photochemistry of vision

Philip J. M. Johnson[1], Alexei Halpin[1], Takefumi Morizumi[2], Valentyn I. Prokhorenko[3], Oliver P. Ernst[2,4] and R. J. Dwayne Miller[1,3]*

The role of vibrational coherence—concerted vibrational motion on the excited-state potential energy surface—in the isomerization of retinal in the protein rhodopsin remains elusive, despite considerable experimental and theoretical efforts. We revisited this problem with resonant ultrafast heterodyne-detected transient-grating spectroscopy. The enhanced sensitivity that this technique provides allows us to probe directly the primary photochemical reaction of vision with sufficient temporal and spectral resolution to resolve all the relevant nuclear dynamics of the retinal chromophore during isomerization. We observed coherent photoproduct formation on a sub-50 fs timescale, and recovered a host of vibrational modes of the retinal chromophore that modulate the transient-grating signal during the isomerization reaction. Through Fourier filtering and subsequent time-domain analysis of the transient vibrational dynamics, the excited-state nuclear motions that drive the isomerization reaction were identified, and comprise stretching, torsional and out-of-plane wagging motions about the local C_{11}=C_{12} isomerization coordinate.

But our key point

Natural Processes (photosynthesis, vision) are induced by incoherent solar/lunar light, whereas laboratory experiments use fast coherent laser pulses .

Dramatically different results, e.g. for isolated molecules:

Pulsed lasers induce coherences (time evolution); Whereas, after some time, Incoherent light produces stationary states (no time evolution). Hence, no discussion – after some time, there are no time evolving coherences. (like thermal bath relaxation)

See Jiang & Brumer, JCP 94, 5833 (1991); Valkunas & Mancal, New J Phys 12, 065044 (2010); Hoki & Brumer, Proc Chem 3, 122 (2011); Brumer & Shapiro, PNAS 109, 19575 (2012); Kassal, Yuen-Zhou & Rahimi-Keshari JPCL 4, 362 (2013); Pachon & Brumer, J. Math Phys 55, 010103 (2014); Cao group ArXiv 1408.5385; Tscherbul & Brumer, Phys Rev A 89, 013423 (2014); Sadeq and Brumer, JCP 140, 074104 (2014); Tscherbul & Brumer, JPCA 118, 3100 (2014); Tscherbul & Brumer, PRL 113, 113601 (2014); Tscherbul & Brumer JCP 142, 104107 (2015) and PCCP 17, 30904 (2015); Dodin, Tscherbul and Brumer, J. Chem. Phys. 144, 244108 (2016).

So the laser and solar light are very different and

Coherent Pulsed laser experiments –
produce transient dynamics.

Nature operates in steady state with incoherent light

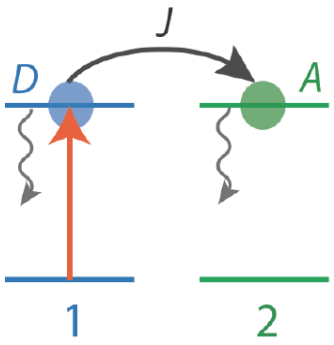
Are laboratory observed coherences relevant to Nature?

Approach: minimal models – analytical solutions

Clear identification of essential physics
System parameters dependence clear and concise

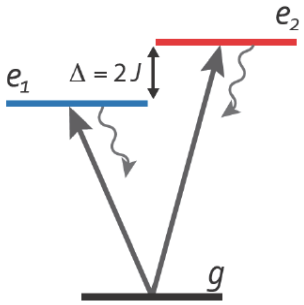
E.g. energy transport in a dimer

Photosynthetic dimer



site basis

$$|g_1 g_2\rangle,\ |e_1 g_2\rangle,\ |g_1 e_2\rangle,\ |e_1 e_2\rangle$$

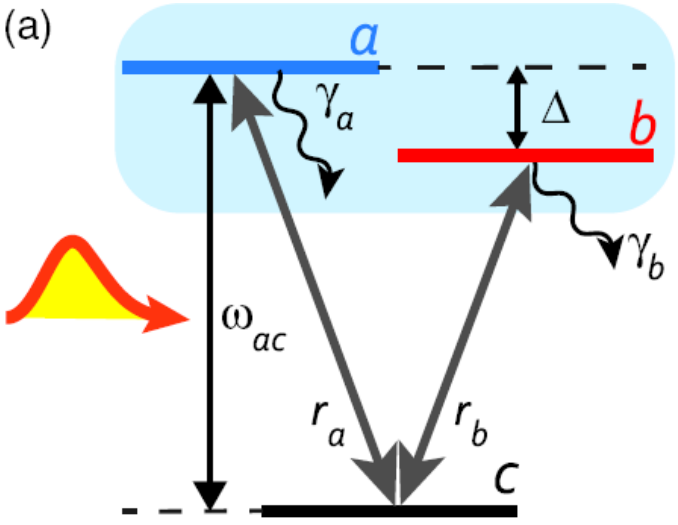


eigenstate basis

$$|e_1\rangle = \frac{1}{\sqrt{2}}\left(|e_1 g_2\rangle + |g_1 e_2\rangle\right)$$

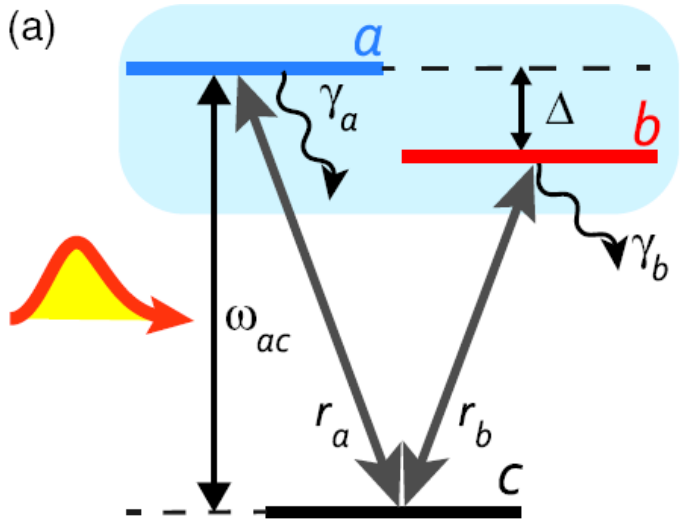
$$|e_2\rangle = \frac{1}{\sqrt{2}}\left(|e_1 g_2\rangle - |g_1 e_2\rangle\right)$$

Consider minimal model of dimer excitation with incoherent solar light



Include spontaneous emission to allow closely spaced levels, include external environment

Build and solve completely positive Nonsecular Master equation to deal with dynamics and coherences

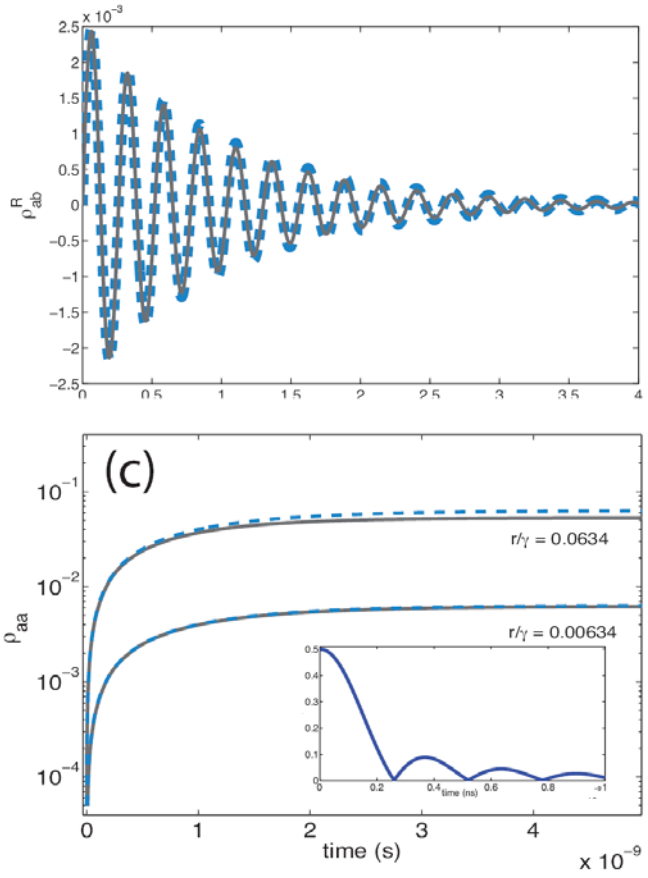


T. Tscherbul and P. Brumer,
Phys. Rev. Lett. 113, 113601 (2014);
A. Dodin, T. Tscherbul and P. Brumer,
J. Chem. Phys. 144, 244108 (2016)

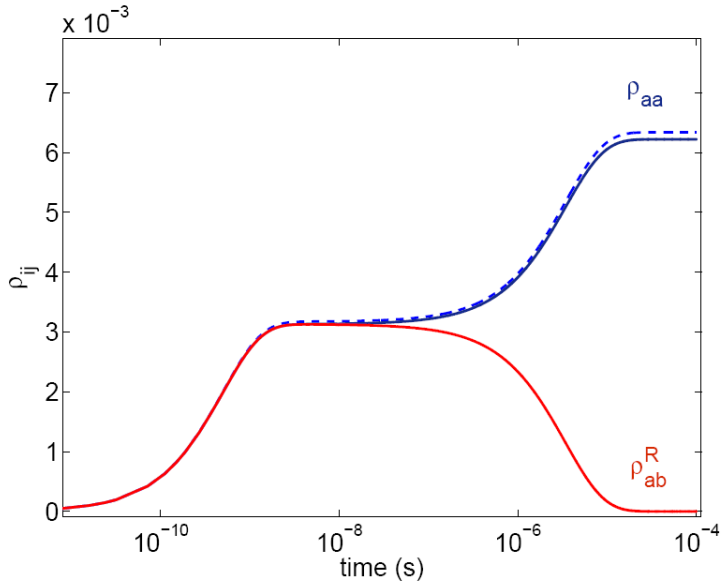
Sample results for sudden turn-on (resembles ultrafast pulse)

E.g., two limits: $\Delta/\gamma \gg 1$ and $\Delta/\gamma \ll 1$ (Analytic)

"Small molecule" case $\Delta/\gamma \gg 1$



"Big molecule" $\Delta/\gamma \ll 1$



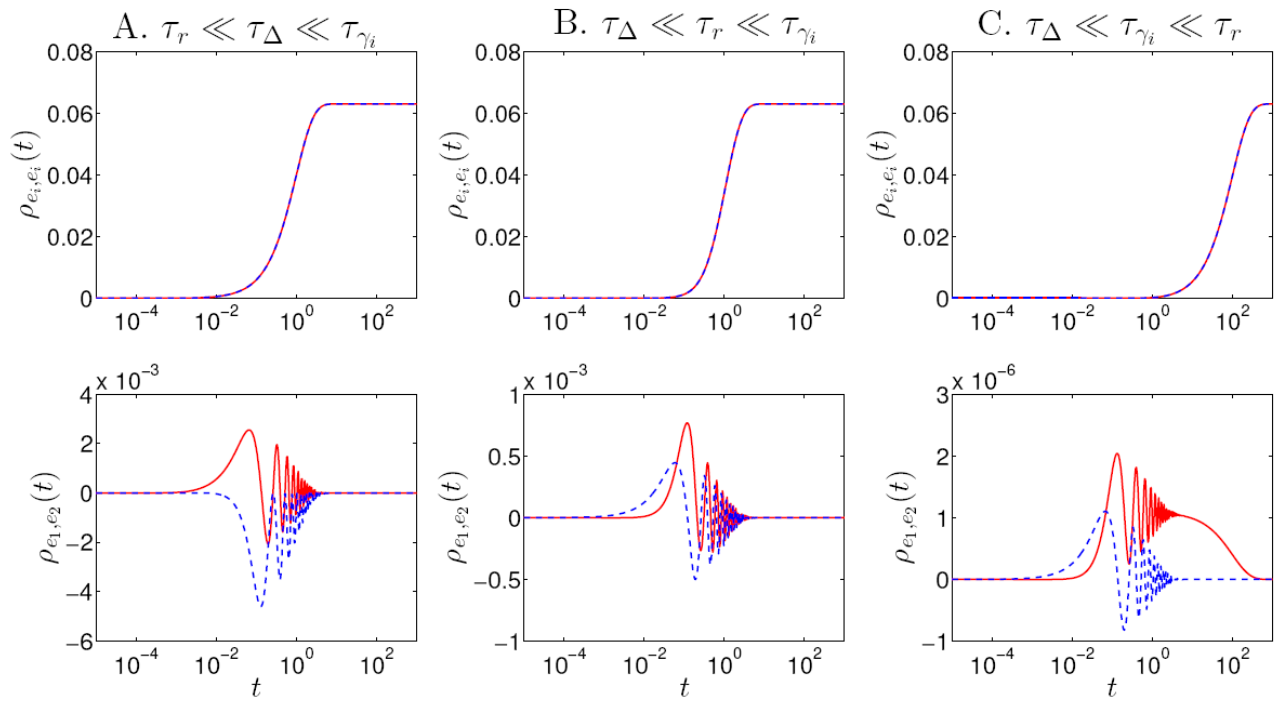
Hence – sudden turn-on (like pulses) produces two types of coherences

But are they important?

After all -- natural turn in is slow!

So -- designed new theory for slow turn on of incoherent light
[Dodin, Tscherbul and Brumer, J. Chem. Phys. 145, 244313 (2016)]

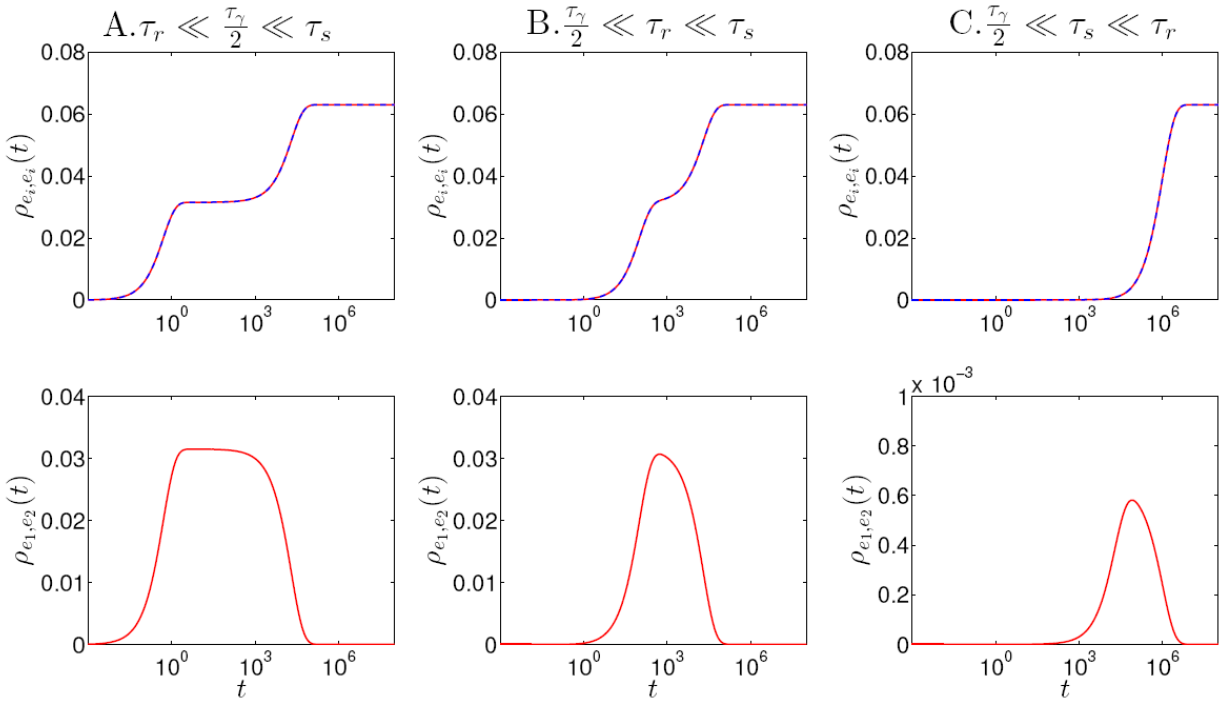
Oscillatory signals ("small molecule" regime)



Note scale reduction—

Fig. 4. Evolution of populations and coherences of an underdamped V-system ($\frac{\Delta_p}{\bar{\gamma}} \gg 1$) evaluated with aligned transition dipole moments ($p = 1$). Here $\gamma_1 = 1.0 = \gamma_2 = \gamma$ and $\Delta = 24.0$. Three different turn on regimes are shown here. Panels A show the ultrafast turn on of the field with $\tau_r = 0.024\tau_\Delta$ while Panels B and C show the intermediate ($\alpha = 24\tau_\Delta$) and slow ($\alpha = 100\tau_\gamma$) turn on regimes respectively. Note the difference in y-axis scales for the coherence plots. Solid red lines indicate the real part of the coherence $\rho^R_{e_1e_2}$ with the imaginary part $\rho^I_{e_1e_2}$ indicated by the dashed blue line.

Long time coherences regime (closely spaced energy levels excited)



Note scale reduction –

Fig. 3. Evolution of populations and coherences of an overdamped V-system ($\frac{\Delta_p}{\bar{\gamma}} \ll 1$) evaluated with aligned transition dipole moments ($p = 1$). Here $\gamma_1 = 1.0 = \gamma_2$ and $\Delta = 0.001$. Three different turn on regimes are shown. Panels A show the ultrafast turn on of the field with $\tau_r = \times 10^{-3}\tau_\gamma$ while Panels B and C show the intermediate ($\tau_r = 100\tau_\gamma = 5 \times 10^{-5}\tau_s$) and slow ($\tau_r = 20\tau_s$) turn on regimes, respectively. Note the difference in y-axis scales for the different coherence plots.

Hence --- for systems in biology – light induced coherences Are never generated due to the natural turn-on times of the light

Analytic conditions obtained : (Defines constraints on both biological and devices to utilize coherences)

T = time to turn on radiation (e.g. sunrise)

t_Δ = typical period of system dynamics

t_γ = decay time due to environment or spontaneous emission

Conditions for survival of oscillatory coherences (widely spaced energy levels; e.g. 100 cm^{-1}):

$T < t_\Delta < t_\gamma$

Not biologically relevant! E.g. $T < t_\gamma$ implies turn on must be faster than environmental relaxation times (e.g. ps to ns)** Practically? Think about chopping the light??

** Isolated incident photons arriving at widely spaced times is an incorrect view.

T = time to turn on radiation (e.g. sunrise)

t_Δ = typical period of system dynamics

t_γ = decay time due to environment or spontaneous emission

Conditions for survival of stationary coherences (very closely spaced energy levels; e.g. vibrations in big molecule):

$t_\Delta >> t_\gamma$ (o.k. implies close energy levels)

$t_\Delta^2 > t_\gamma T$

possible– under consideration

But some samples (just spontaneous emission decay). Say want only 1% coherence/populations .

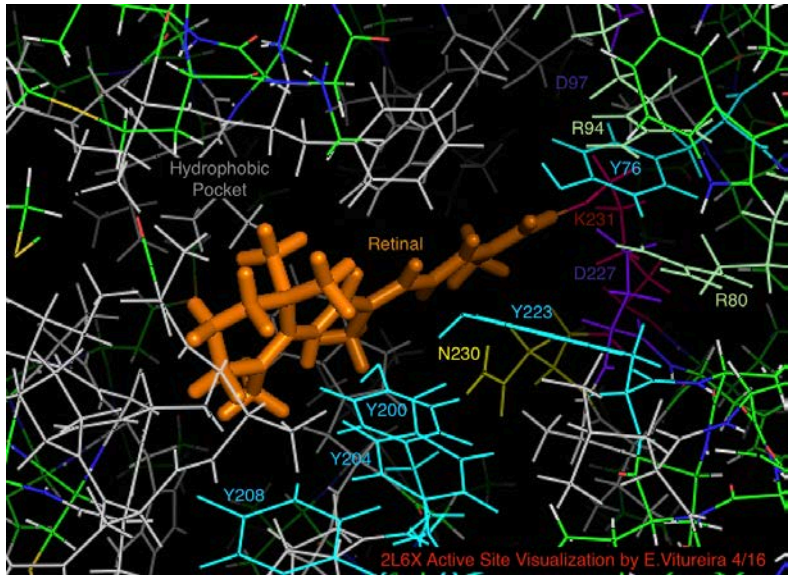
For electronic excitation in FMO --- need faster than 10 ns. turn on.

For turn-ons that are slower than 1 ms, states closer than 0.9 cm^{-1} are coherently excited. Clearly suppressed in practice.

SO MUST DO STEADY STATE STUDIES

Consider then Retinal isomerization in vision – first step
Also “Rhodopsin based form of Photosynthesis” --- relies on cis/trans or trans/cis isomerization of retinals, e.g. proteorhodopsins in marine Proteobacteria – like bacteriorhodopsin undergoes all trans to cis isomerization and serves a proton pump. Also Retinoic acid in biological cell differentiation Many others

See, e.g. “Biophysics: Searching for Principles”, W. Bialik, Princeton University Press, 2012 --- huge focus



Challenging theoretical/computational problems

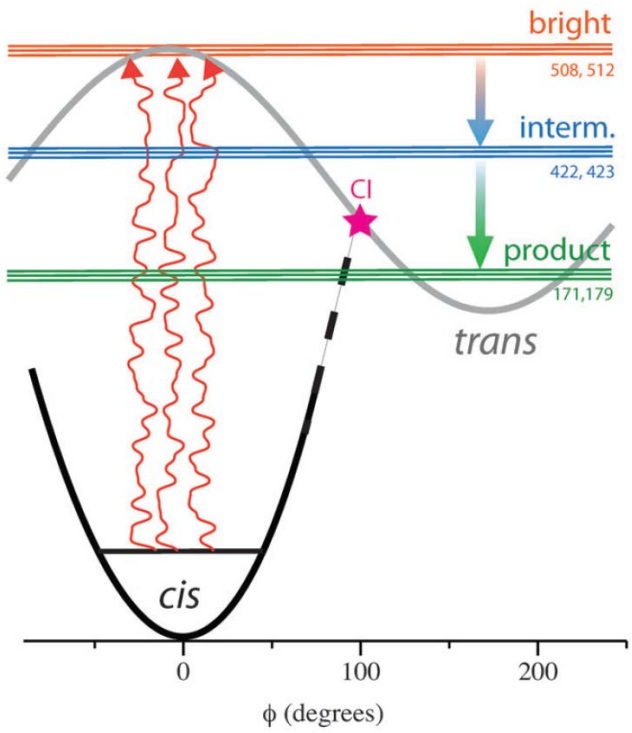
1. **Are there quantum coherences in natural Retinal isomerization process— i.e. when irradiated with natural incoherent light? and with slow turn on?**

2. **If there are, do they matter to the bio process?**

3. **What is the role of the environment in the participation of coherences (if they are there)**

4. **Rates (“as fast as nature can allow”) – what are rates in nature?**

And a “real” case: Retinal, as an example. Are (Fano) coherences:important?



$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\rho}_{\mathrm{full}} = -i\left[\hat{H}, \hat{\rho}_{\mathrm{full}}\right],$$

$$\hat{H} = \hat{H}_{\mathrm{S}} + \hat{H}_{\mathrm{S-rad}} + \hat{H}_{\mathrm{S-ph}} + \hat{H}_{\mathrm{rad}} + \hat{H}_{\mathrm{ph}}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\rho} = -i\left[\hat{H}_{\mathrm{S}}, \hat{\rho}\right] + \mathcal{L}_{\mathrm{rad}}[\hat{\rho}] + \mathcal{L}_{\mathrm{ph}}[\hat{\rho}],$$

In our case, H_{S} in eqn (1) is the two-state two-mode (TSTM) model Hamiltonian of the retinal chromophore[28,30]

$$\hat{H}_{\mathrm{S}} = \sum_{n,n'}\left[\left(\hat{T} + E_n + (-1)^n\frac{1}{2}\tilde{V}_n(1-\cos\phi) + \omega x^2\Big/2 + \kappa x\delta_{n,1}\right)\delta_{nn'} + \lambda x(1-\delta_{nn'})\right]|n\rangle\langle n'| \qquad (3)$$

which includes the key degrees of freedom involved in retinal photoisomerization: the low-frequency tuning mode $\phi \in [-\pi/2, 3\pi/2]$ and the high-frequency stretching mode x. As pictured in Fig. 1(a), the range of $\phi \in [-\pi/2, \pi/2]$ corresponds to the *cis*-isomer of retinal and $\phi \in [\pi/2, 3\pi/2]$ – to the *trans*-isomer. In

Master Equation Computational Issues (just comments)

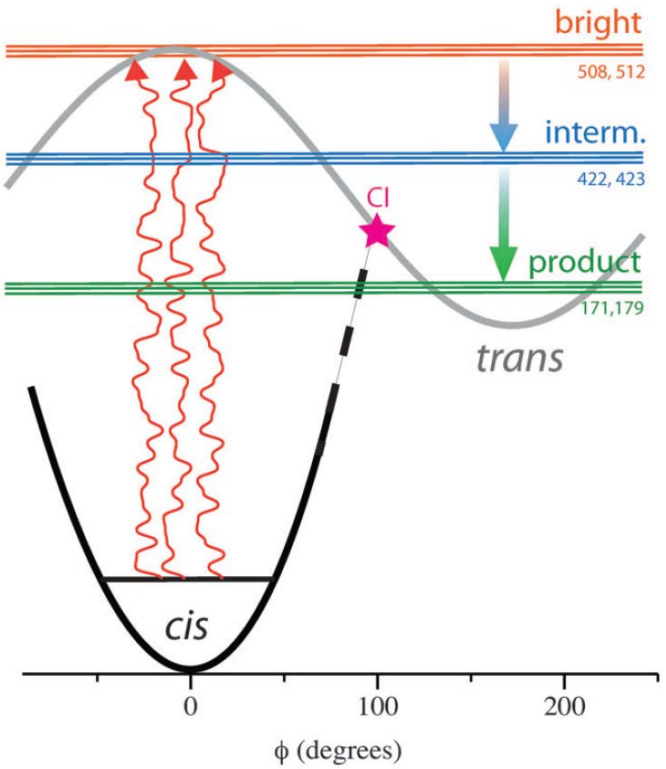
Require Completely Positive Master Equations

e.g. See Alicki and Lendi, “Quantum Dynamical Semigroups and Applications”, Springer, 2007

Issue of Secular vs. Nonsecular Master Equations

e.g. A. Dodin, T. Tscherbul, R. Alicki, A. Vutha and P. Brumer PRA 97, 013421 (2018)

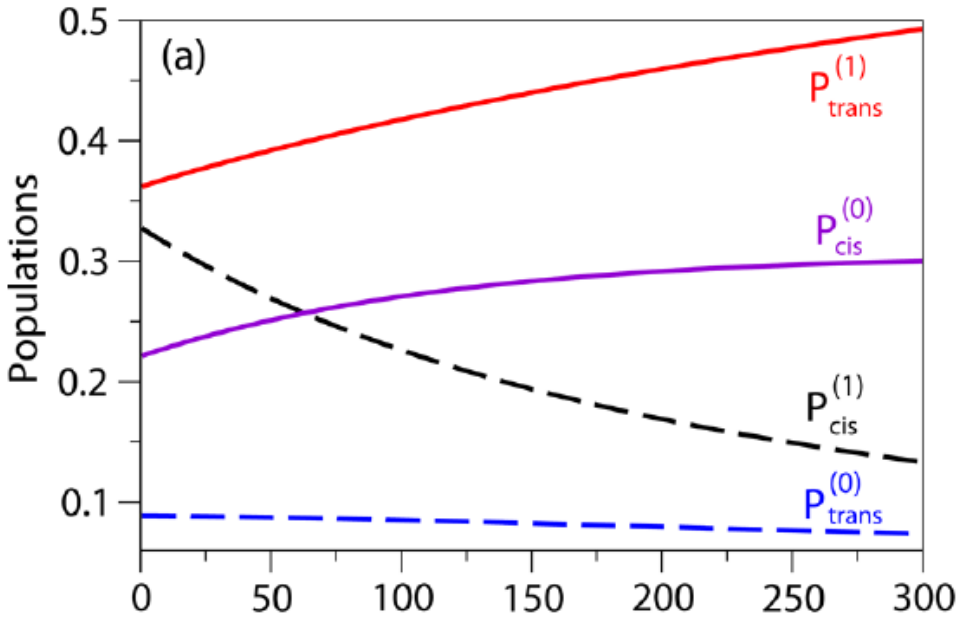
Eigenstate Model of Retinal Dynamics (standard two mode)



Note Delta/Gamma > 1
correct due active Franck-Condon modes

Steady state approach gives perfect quantum yield (both experimental and pulsed laser results)

First, sudden turn-on --- do coherences survive? Relevant?



and $|\psi_1\rangle$. An important quantity that characterizes photoreaction efficiency is the quantum yield defined as the fraction of the *trans*-product population relative to the overall excited-state population.

$$Y(t) = \frac{P^{(1)}_{trans}(t)}{P^{(0)}_{cis}(t) + P^{(1)}_{trans}(t)}. \qquad (14)$$

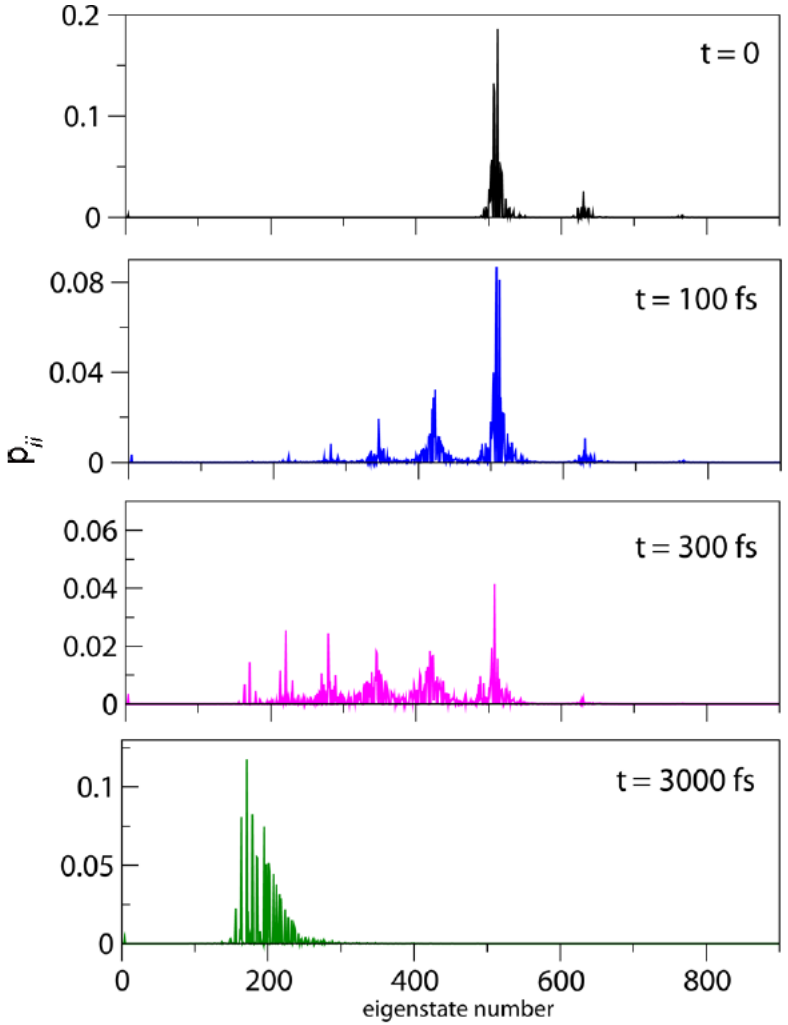
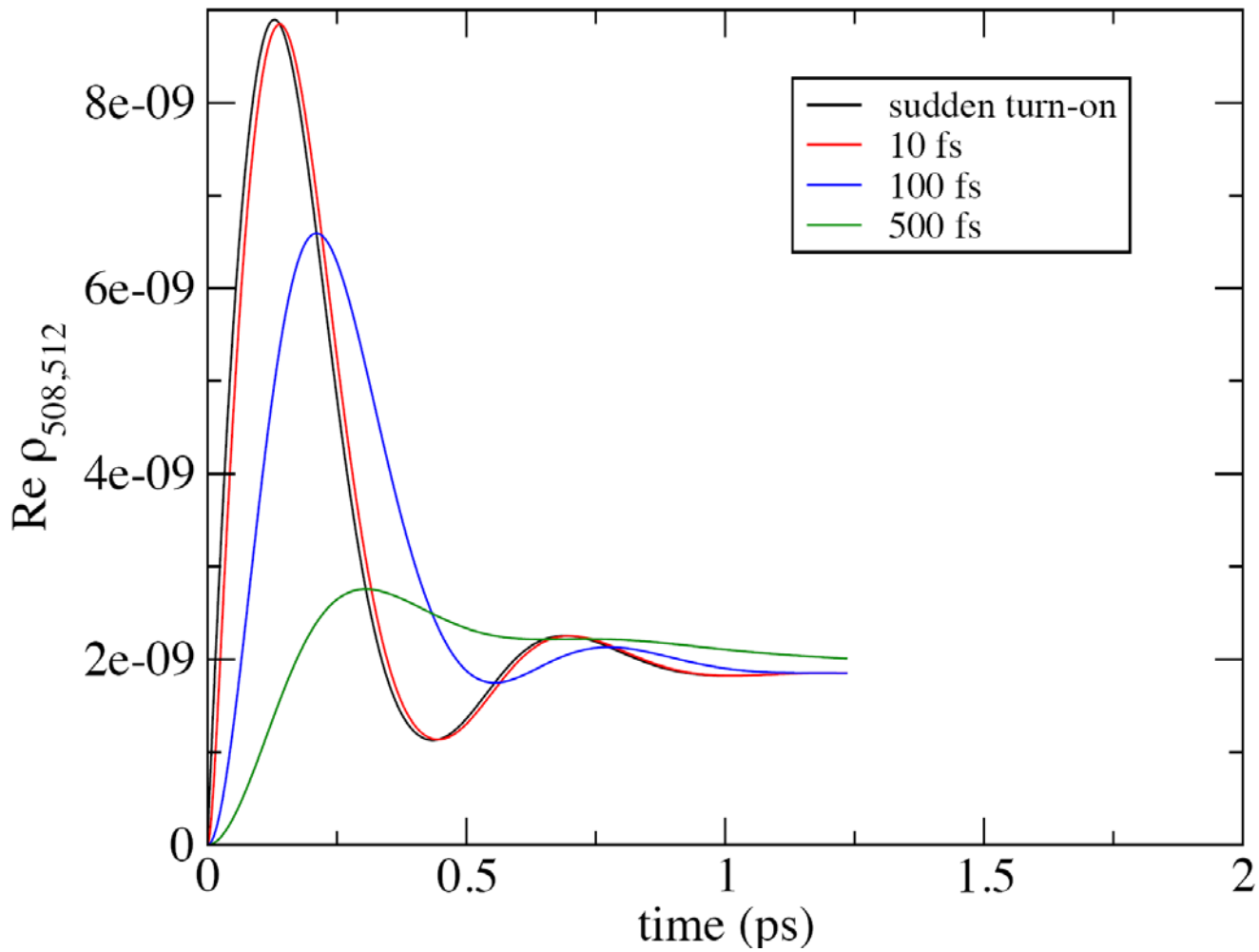


Figure 5. Snapshots of eigenstate populations $\rho_{ii}(t)$. At $t = 0$, the bright eigenstates (mostly 512, 507, and 508) are populated by fully incoherent, impulsive FC excitation (see eq 6). At later times, interaction with the bath causes the population of the bright states to decay through several cascades (middle panels). The resulting steady-state eigenstate distribution is plotted in the lowermost panel.

Typical coherence contribution (sudden turn-on – black) significant over 400 fs, with long time (bath-induced) stationary coherence.



And the effect of the light-induced coherences?

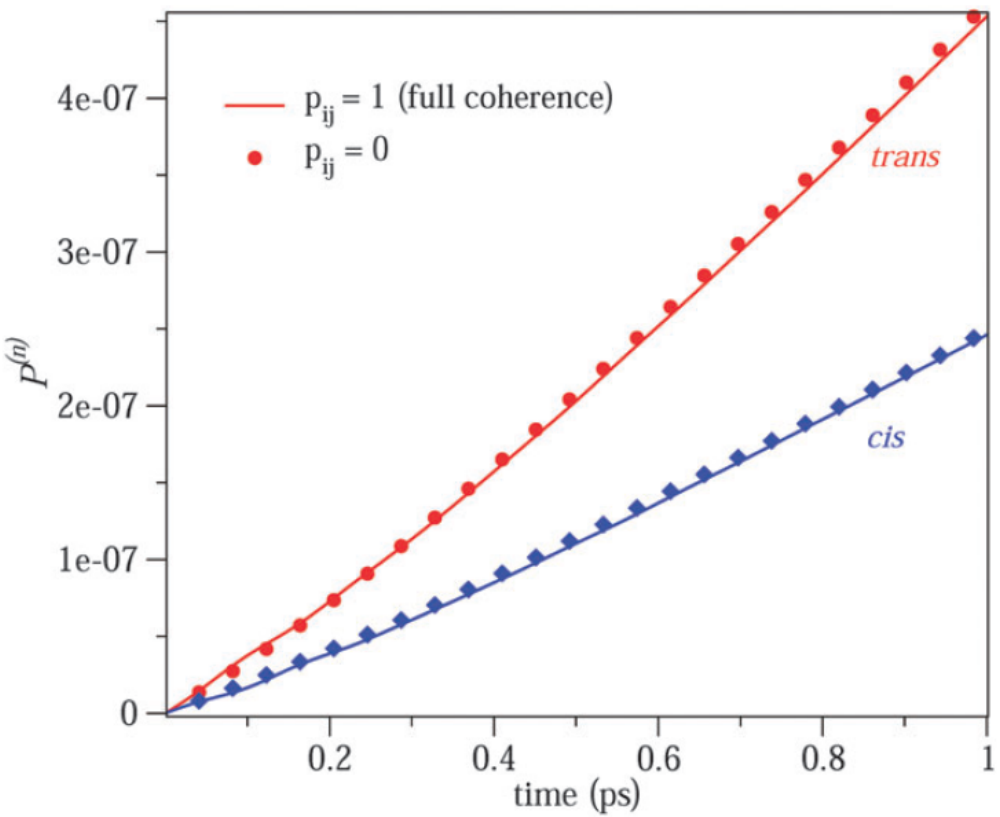


Fig. 3 Time evolution of *cis* and *trans* photoproduct populations: parallel transition dipole moments (full lines), orthogonal transition dipole moments (symbols).

No sig. effect on isomerization!—

I.e. these coherences do not matter to the natural process

Why?
Systems with weaker coupling to bath?

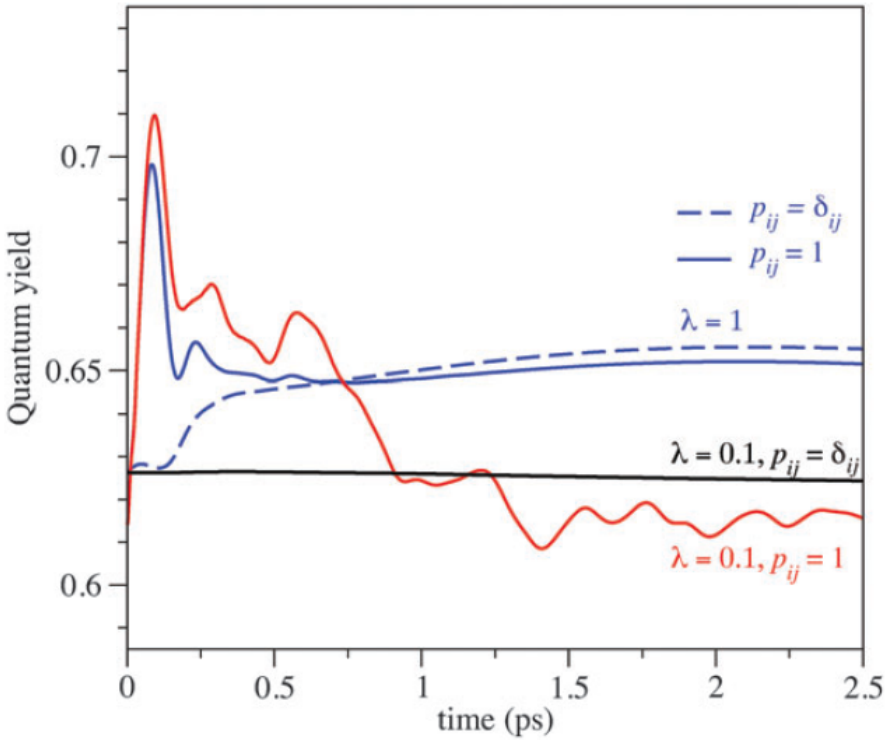


Fig. 5 Time evolution of the photoreaction quantum yield calculated for $\lambda = 1$ and 0.1, and for parallel and orthogonal transition dipole moments ($p_{ij} = \delta_{ij}$ *vs.* 1). Each curve is marked by the corresponding values of λ and p_{ij}.

$$J_\alpha(\omega) = \eta_\alpha e^{-\omega/\omega_{c\alpha}},$$

Multiply by scaling lambda

Bath effect relates to role and survival of the stationary bath induced coherences.

and $|\psi_1\rangle$. An important quantity that characterizes photoreaction efficiency is the quantum yield defined as the fraction of the *trans*-product population relative to the overall excited-state population.

$$Y(t) = \frac{P^{(1)}_{trans}(t)}{P^{(0)}_{cis}(t) + P^{(1)}_{trans}(t)}. \qquad (14)$$

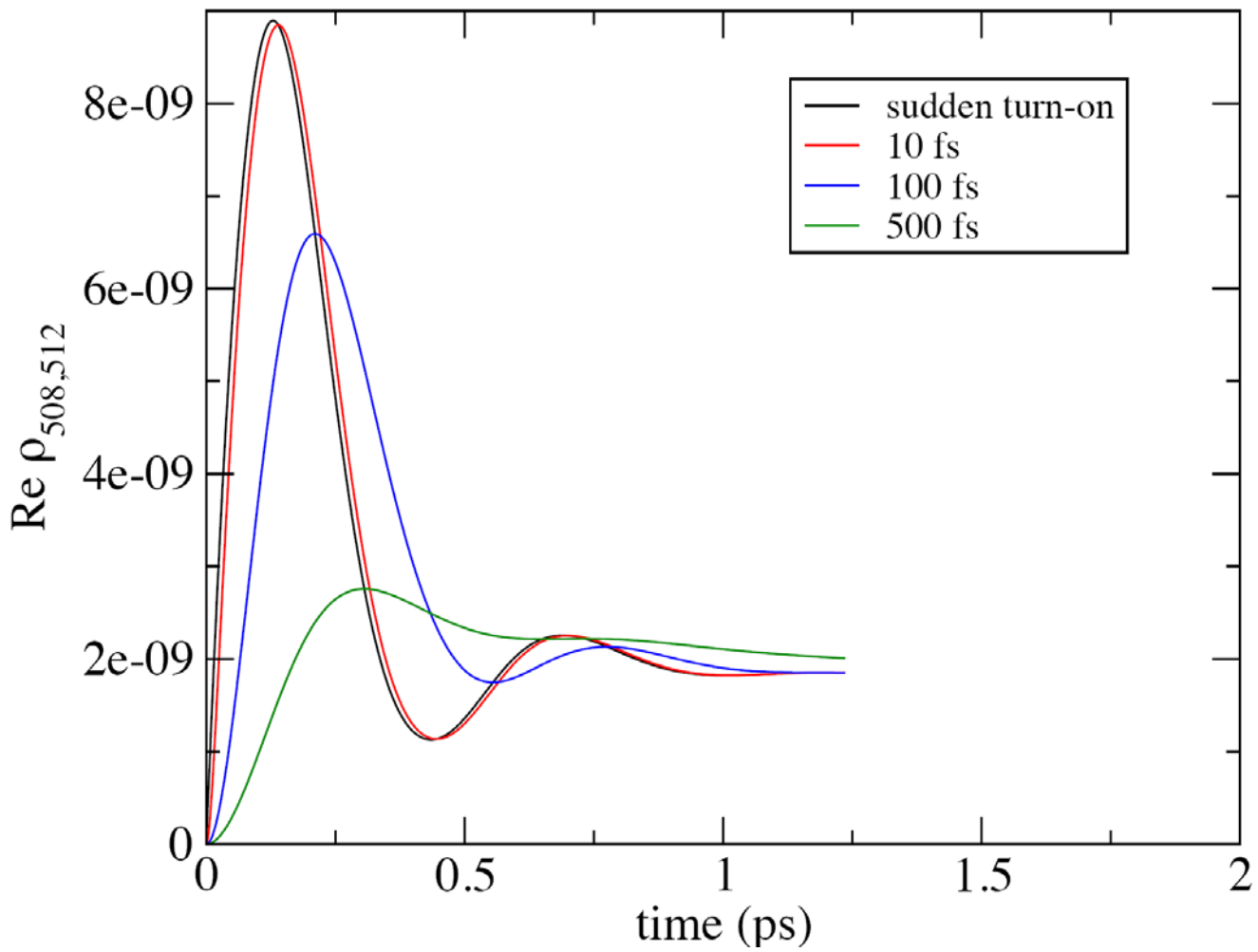
Hence --- we see interesting effect on quantum yield due to the nature of the system-bath coupling in altering the stationary coherences.

…

But – same question –

above assumes sudden excitation

--- and slow turn on, as in nature?



Oscillatory coherences disappear as turn on slows down (even here is fast)—

However, stationary long term coherence survives (“transport” issue)

Why persist in retinal --- it is a transport process (as are many biological processes).

Consider model (note decay channels; i.e. input and output)

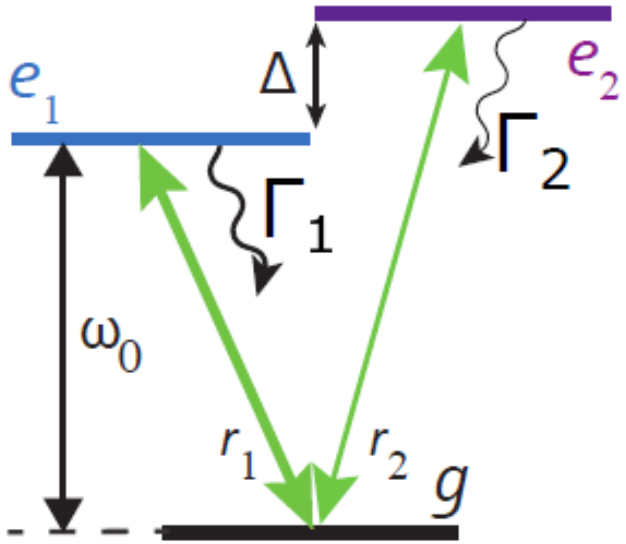


FIG. 7: Schematic illustration of analytical Bloch-Redfield model for steady state coherences. The ground to excited state manifold splitting is given by a transition frequency of ω_0 while splitting between the excited states is given by Δ. The incoherent photon bath drives absorption and stimulated emission between states $|g\rangle$ and $|e_i\rangle$ at a rate r_i while the phonon bath drives non-radiative decay at a rate Γ_i.

Say for equal excitation rates, then coherences survive as:

$$\lim_{t\to\infty} \rho^R_{1,2}(t) = \frac{\sqrt{\Gamma_1\Gamma_2}}{\Gamma_1+\Gamma_2}\left(\frac{(\sqrt{\Gamma_1}-\sqrt{\Gamma_2})^2}{(\sqrt{\Gamma_1}-\sqrt{\Gamma_2})^2+2\Delta}\right)$$

$$\lim_{t\to\infty} \rho^I_{1,2}(t) = -\frac{\Delta}{r+\frac{1}{2}(\Gamma_1+\Gamma_2)} \lim_{t\to\infty} \rho^R_{1,2}(t)$$

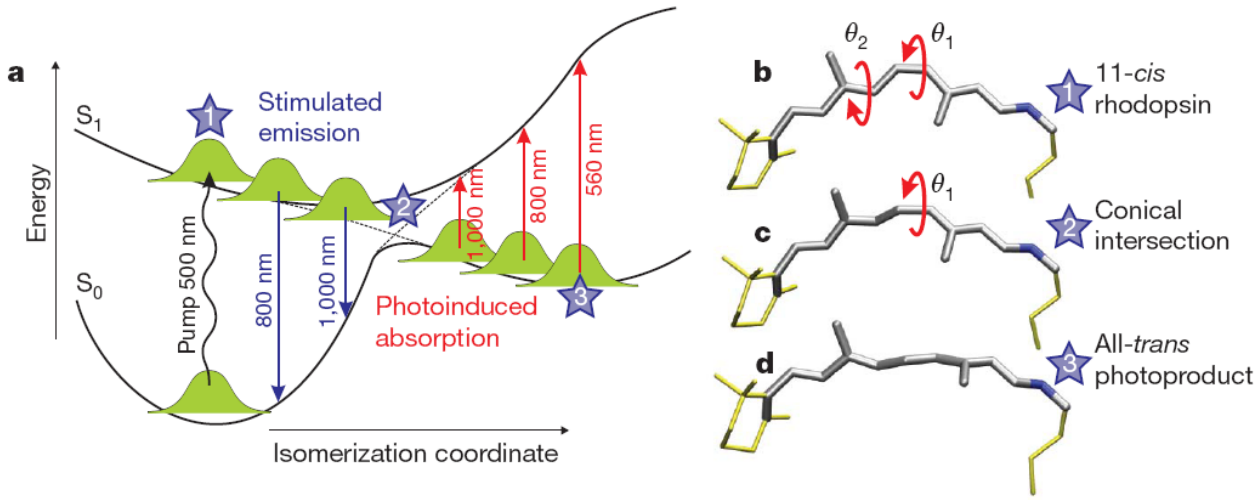
Hence interesting new physics in the existence and dependence on the off-diagonal stationary coherences1

But rates?

E.g. Literature: “Rate” of cis-trans isomerization in Retinal is < 100 fs.

But “rate” is function of circumstance/ensemble, i.e. there is not single rate.
(See Shapiro & Brumer, Quantum Control of Molecular Processes, Wiley, 2012)

For example, retinal rates of < 100 fs are for transient pulsed excitation. I.e. for



What about natural light induced steady state ?
Early treatment: K. Hoki and P. Brumer, Procedia Chem. 3, 122 (2011)

Long time process, steady state rate, quantum effects
Time Dependent Master Equation difficult
--- we built new approach

$$\hat{\chi}(t) = \hat{O}(t) - \mathrm{Tr}(\hat{\rho}_s \hat{O})\hat{\mathbb{1}}$$

$$\hat{\rho}_s = \hat{\rho}(t \to \infty)$$

$$\partial_t \hat{\rho}_s \equiv \hat{\mathcal{L}} \hat{\rho}_s = \hat{0},$$

Introduce

$$\langle \hat{\chi}(t) \rangle = \mathrm{Tr}[\hat{\rho}_0 \hat{\chi}(t)],$$ (progress variable)

$$I_n \equiv \int_0^\infty dt\ t^n \langle \hat{\chi}(t) \rangle$$ (moments)

Introduce::

$$\hat{\mathcal{L}}\hat{A}_n = \hat{c}_n \equiv \begin{cases} \hat{\rho}_0 - \hat{\rho}_s, & \text{if } n = 0 \\ \hat{A}_{n-1} - \mathrm{Tr}(\hat{A}_{n-1})\hat{\rho}_s, & \text{if } n \neq 0. \end{cases}$$

And find:

$$\frac{d}{dt}\mathrm{Tr}[\hat{A}_n\hat{\chi}(t)] = \begin{cases} \langle\hat{\chi}(t)\rangle\,, & \text{if } n = 0 \\ \mathrm{Tr}[\hat{A}_{n-1}\hat{\chi}(t)], & \text{if } n \neq 0. \end{cases}$$

$$I_n = \int_0^\infty dt\; t^n \frac{d}{dt}\mathrm{Tr}[\hat{A}_0\hat{\chi}(t)] \quad = (-1)^{n+1}\; n!\; \mathrm{Tr}[\hat{A}_n\hat{\chi}].$$

Find A's ➔ Find I's ➔Moments then used to reconstruct the time dependence

Method is very fast (hours vs days)

E.g. Retinal reconstructed dynamics --- sudden turn-on

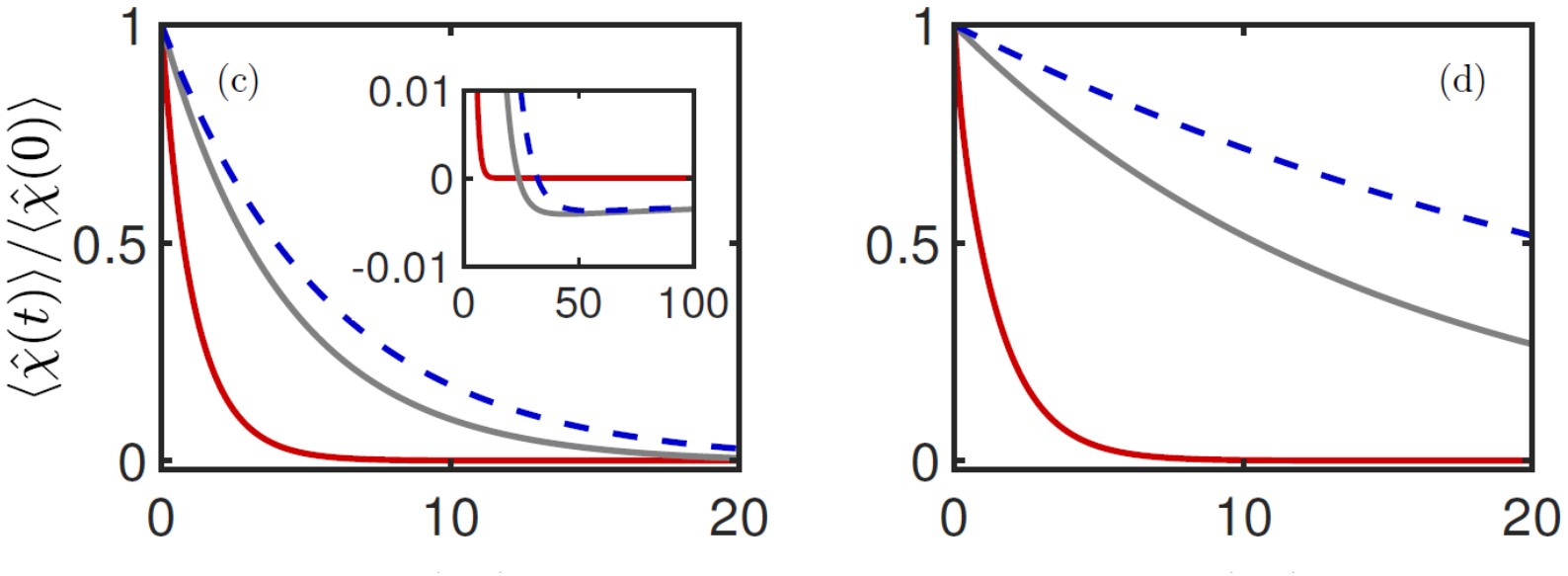


Figure 4: (a) Comparison of simulated (solid red) and predicted (dashed blue) values of the forward reaction time, $\tau \equiv k_f^{-1}$ in the secular approximation for $C = 1$. Inset: enlarged view for early times. (b) As in (a), but without the secular approximation. (c) Reconstructed normalized progress variable for $C = 1$ (solid red), $C = 10^{-5}$ (solid grey), and $C = 10^{-7}$ (dashed blue), in the secular approximation. Inset: Long-time behaviour. (d) As in (c), but without the secular approximation.

And resultant forward reaction times:

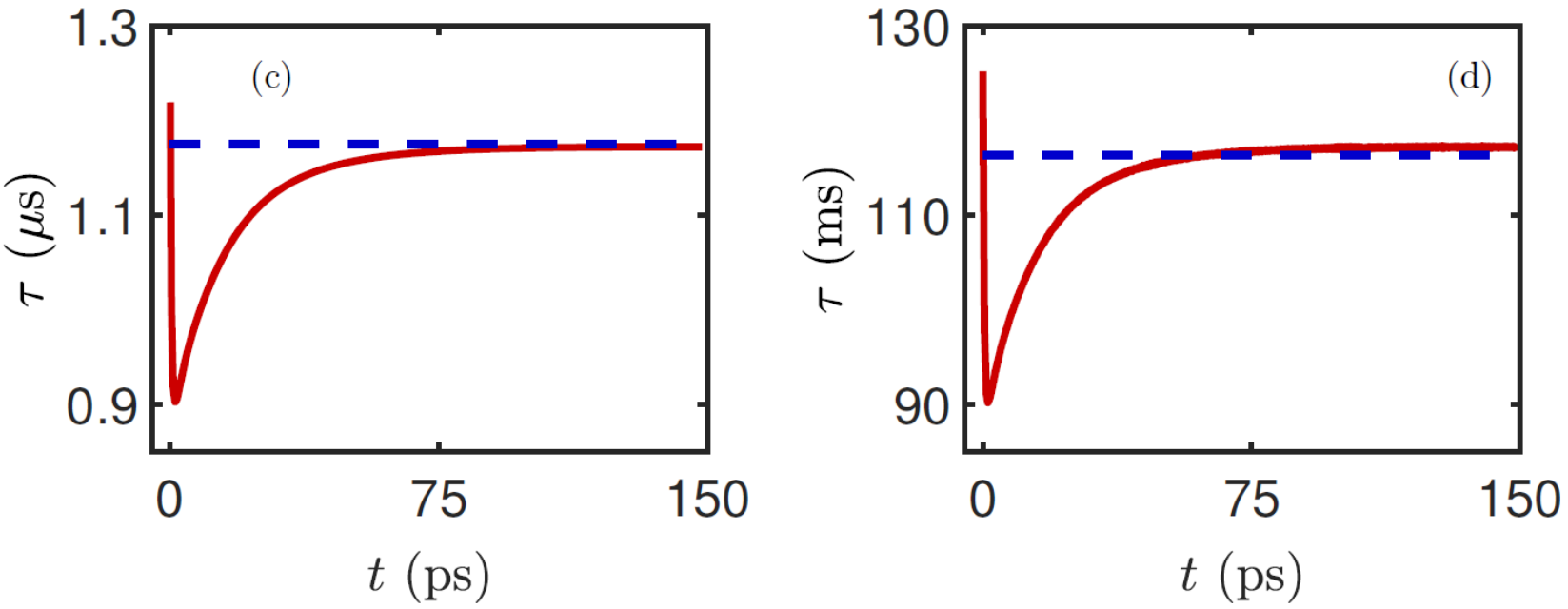


Figure 3: (a) Reconstructed normalized progress variable for $C = 1$ (solid red), $C = 10^{-5}$ (solid grey), and $C = 10^{-7}$ (dashed blue), in the secular approximation. Inset: Long-time behaviour. (b) As in (a), but with full coherences. (c) Comparison of simulated (solid red) and predicted (dashed blue) values of the forward reaction time, $\tau \equiv k_f^{-1}$, for $C = 1$ in the secular approximation. (d) As in (c), but for $C = 10^{-5}$.

Note time scales!! Not fsec
--- excitation is rate determining step

Hence natural rates are far far longer than the transient ~100 fsec transient pulsed rates that evoke lots of excitement

Also crucial result regarding rates --- partitioning of product into product channels (e.g. return to cis or trans). Strongly affected by system-environmental interaction, and hence will differ across biological cases.

Tools introduced in this study:

Partial secular master equations for electronic excitation with Incoherent light.

Master Equations with time dependent bath.

Master Equations are completely positive and non-secular.

Efficient way to reconstruct dynamics and rates for steady state processes

Work in Progress:

Is system-environment dependence a quantum effect?

If so, of what type? Entanglement?

Is there biological significance with interesting open-system attributes?

Considering wide variety of system-bath biological possibilities
Is there tuning of system-bath to enhance biological function?

Explore with larger computational focus?

Dependence on spectral density

Other challenges being addressed::

Characteristics of light-induced signals that prove quantumness

Biological diversity of rhodopsins and their dependence on system-(protein) environment interaction

Classical vs quantum visual process rates

Role of any initial quantum effects in biology “down the line”.

Benefiting from new experimental studies to build the in-vitro case

Indeed significant note.

Significant underlying lesson for biophysical studies ---:

In-vitro lab studies can be very different than in- vivo.

Hence combined experimental/theoretical effort vital

a. Obtain detailed info from in-vitro experiments

b. Use the results as input to build models for in-vivo that are also (but not the goal!) consistent with in-vitro.

Note significant: "b" generalizes "a" to a new (in-vivo) domain. What you see in "a" need not be what happens in nature!

And here are some new in-vitro studies from which we will benefit -

Interaction of Fixed Number of Photons with Retinal Rod Cells

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(Received 18 December 2013; published 29 May 2014)

New tools and approaches of quantum optics offer a unique opportunity to generate light pulses carrying a precise number of photons. Accurate control over the light pulses helps to improve the characterization of photoinduced processes. Here, we study interaction of a specialized light source which provides flashes containing just one photon, with retinal rod cells of *Xenopus laevis* toads. We provide unambiguous proof of the single-photon sensitivity of rod cells without relying on the statistical modeling. We determine their

ARTICLES
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nature chemistry

Local vibrational coherences drive the primary photochemistry of vision

Philip J. M. Johnson[1], Alexei Halpin[1], Takefumi Morizumi[2], Valentyn I. Prokhorenko[3], Oliver P. Ernst[2,4] and R. J. Dwayne Miller[1,3]*

The role of vibrational coherence—concerted vibrational motion on the excited-state potential energy surface—in the isomerization of retinal in the protein rhodopsin remains elusive, despite considerable experimental and theoretical efforts. We revisited this problem with resonant ultrafast heterodyne-detected transient-grating spectroscopy. The enhanced sensitivity that this technique provides allows us to probe directly the primary photochemical reaction of vision with sufficient temporal and spectral resolution to resolve all the relevant nuclear dynamics of the retinal chromophore during isomerization. We observed coherent photoproduct formation on a sub-50 fs timescale, and recovered a host of vibrational modes of the retinal chromophore that modulate the transient-grating signal during the isomerization reaction. Through Fourier filtering and subsequent time-domain analysis of the transient vibrational dynamics, the excited-state nuclear motions that drive the isomerization reaction were identified, and comprise stretching, torsional and out-of-plane wagging motions about the local C_{11}=C_{12} isomerization coordinate.

frontiers in PSYCHOLOGY
ORIGINAL RESEARCH ARTICLE
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Retinal and post-retinal contributions to the quantum efficiency of the human eye revealed by electrical neuroimaging

*Gibran Manasseh[1], Chloe de Balthasar[1], Bruno Sanguinetti[2], Enrico Pomarico[2], Nicolas Gisin[2], Rolando Grave de Peralta[1] and Sara L. Gonzalez Andino[1,3]**
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The retina is one of the best known quantum detectors with rods able to reliably respond to single photons. However, estimates on the number of photons eliciting conscious perception, based on signal detection theory, are systematically above these values after discounting by retinal losses. One possibility is that there is a trade-off between the limited motor resources available to living systems and the excellent reliability of the visual photoreceptors. On this view, the limits to sensory thresholds are not set by the individual reliability of the receptors within each sensory modality (as often assumed) but rather by the limited central processing and motor resources available to process the constant inflow of sensory information. To investigate this issue, we reproduced the classical experiment from Hetch aimed to determine the sensory threshold in human vision. We combined a careful physical control of the stimulus parameters with high temporal/spatial resolution recordings of EEG signals and behavioral variables over a relatively large sample of subjects (12). Contrarily to the idea that the limits to visual sensitivity are fully set by the statistical fluctuations in photon absorption on retinal photoreceptors we observed that the state of ongoing neural oscillations before any photon impinges the retina helps to determine if the responses of photoreceptors have access to central conscious processing. Our results suggest that motivational and attentional off-retinal mechanisms play a major role in reducing the QE efficiency of the human visual system when compared to the efficiency of isolated retinal photoreceptors. Yet, this mechanism might subserve adaptive behavior by enhancing the overall multisensory efficiency of the whole system composed by diverse reliable sensory modalities.

ARTICLE
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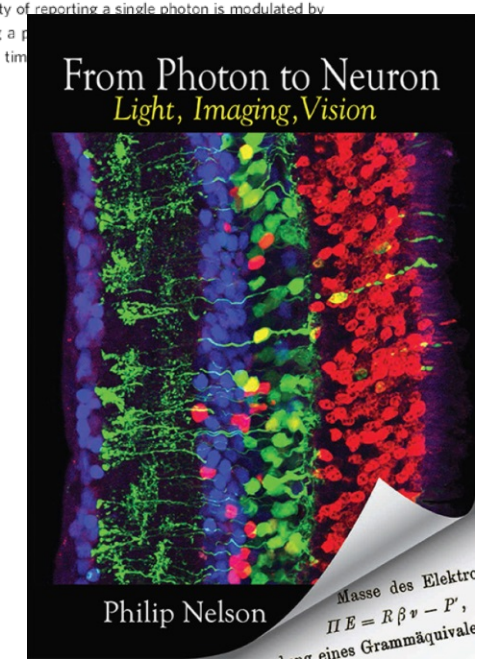
Direct detection of a single photon by humans

Jonathan N. Tinsley[1,2,†,*], Maxim I. Molodtsov[1,2,3,*], Robert Prevedel[1,2,3], David Wartmann[1,†], Jofre Espigulé-Pons[2,4], Mattias Lauwers[1] & Alipasha Vaziri[1,2,3,5]

Despite investigations for over 70 years, the absolute limits of human vision have remained unclear. Rod cells respond to individual photons, yet whether a single-photon incident on the eye can be perceived by a human subject has remained a fundamental open question. Here we report that humans can detect a single-photon incident on the cornea with a probability significantly above chance. This was achieved by implementing a combination of a psychophysics procedure with a quantum light source that can generate single-photon states of light. We further discover that the probability of reporting a single photon is modulated by the presence of an earlier photon, suggesting a p
the effective gain of the visual system on the tim



RESEARCH ARTICLE

Human Visual System as a Double-Slit Single Photon Interference Sensor: A Comparison between Modellistic and Biophysical Tests

Rita Pizzi*, Rui Wang, Danilo Rossetti

Department of Computer Science, University of Milan, Milan, Italy

In summary, systematic study shows:

0. Light induced processes in nature operate in the steady state. This is where studies should be done. – e.g. via pulsed-incoherent approach. (Experimental proposal) --- via our steady state ME approach, etc.

1. The oscillatory coherences observed in pulsed laser experiments are due to the rapid laser pulses used to excite the system.

2. Such coherences are not generated in nature (Even interesting Fano coherences).

3. Natural rates are slow, with absorption of light being rate-determining.

4. Interesting effect to explore for biology , however, are stationary coherences that relate to coupling of a system to the surrounding environment(s). This is also controllable by varying this coupling via alterations in structure. Can affect quantum yield, etc.

5. But pulsed laser experiments provide vital system, system-bath information, crucial for any study.

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