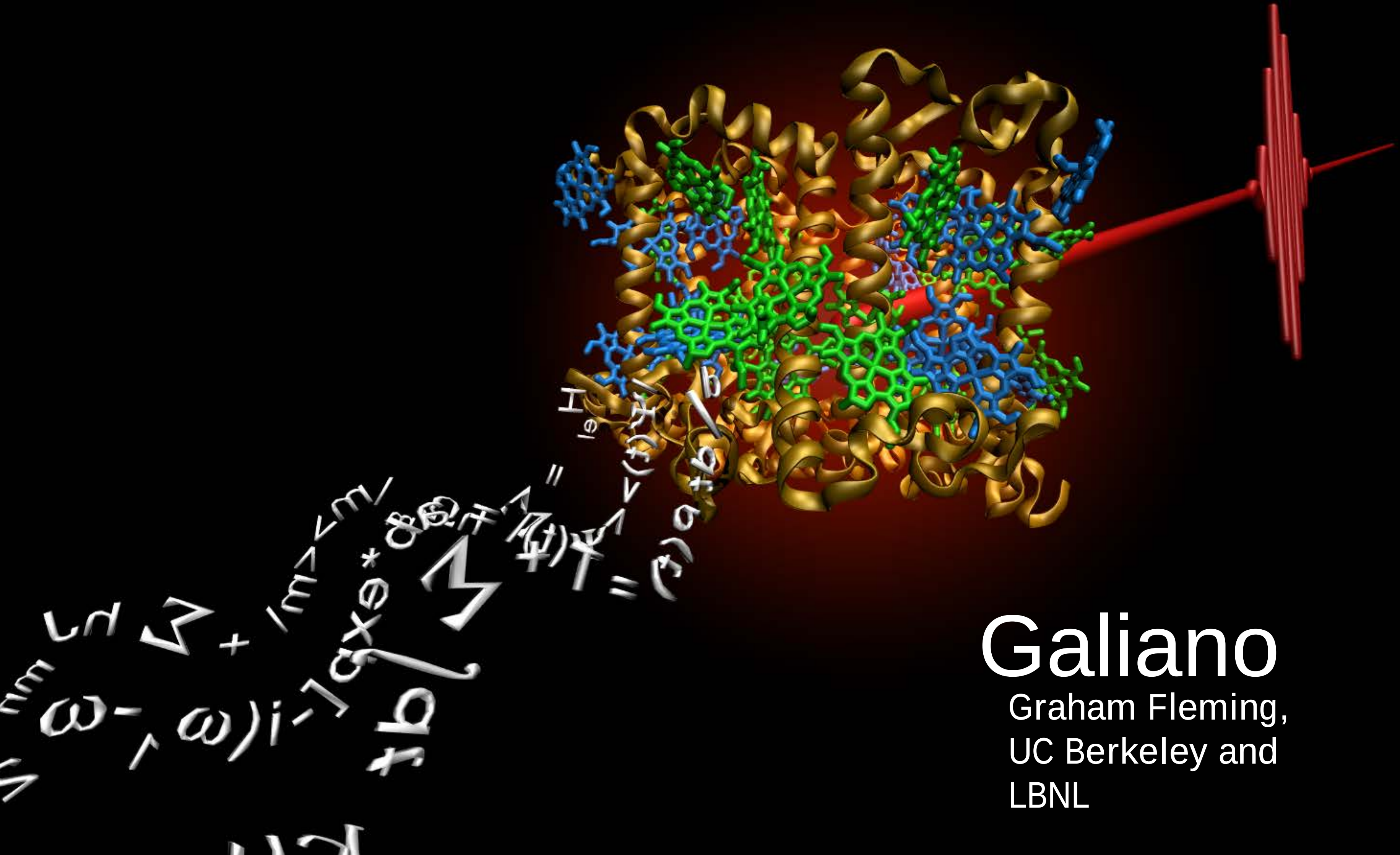
Coherence in Photosynthetic Light Harvesting

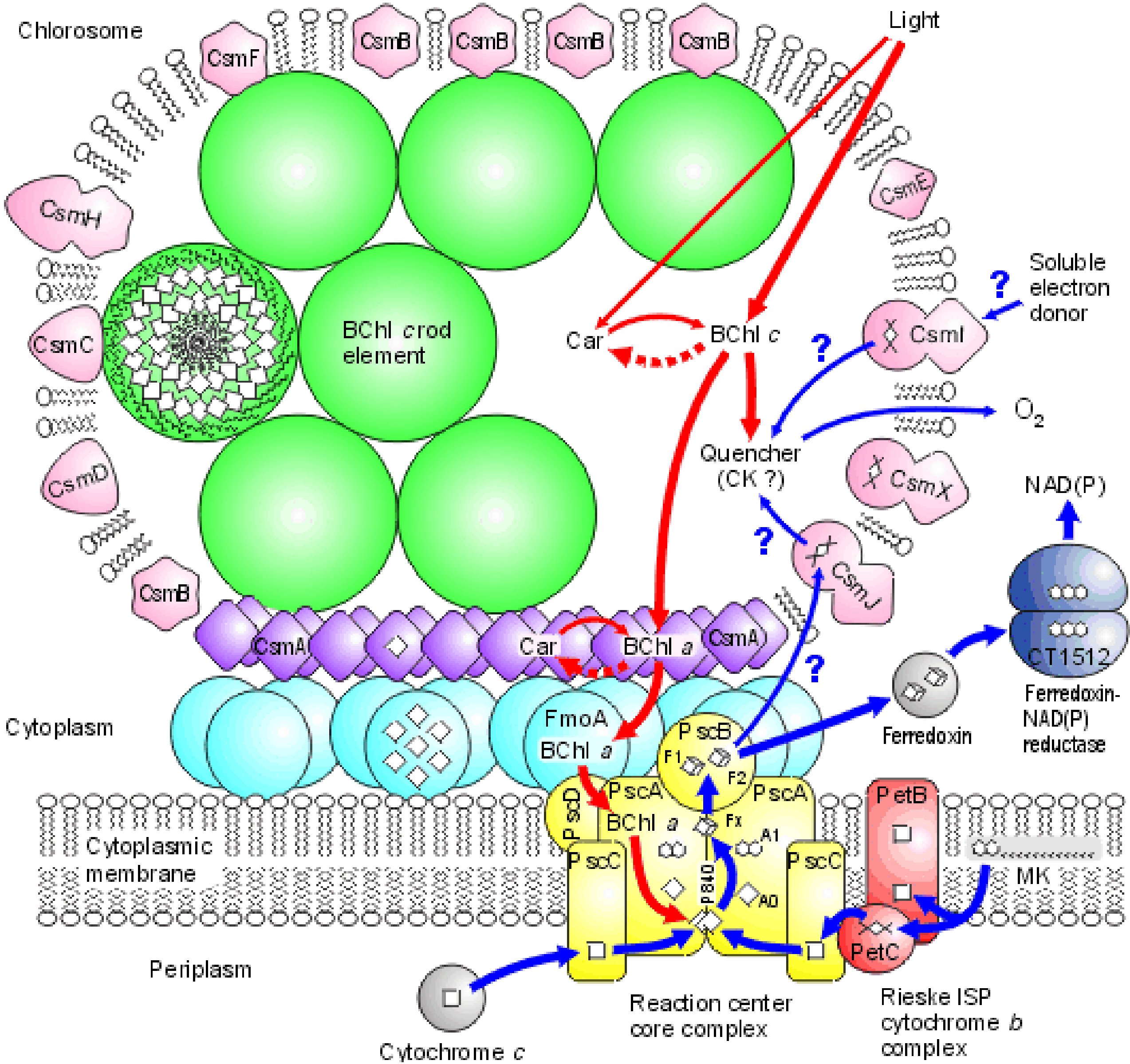


Galiano

Graham Fleming,
UC Berkeley and
LBNL

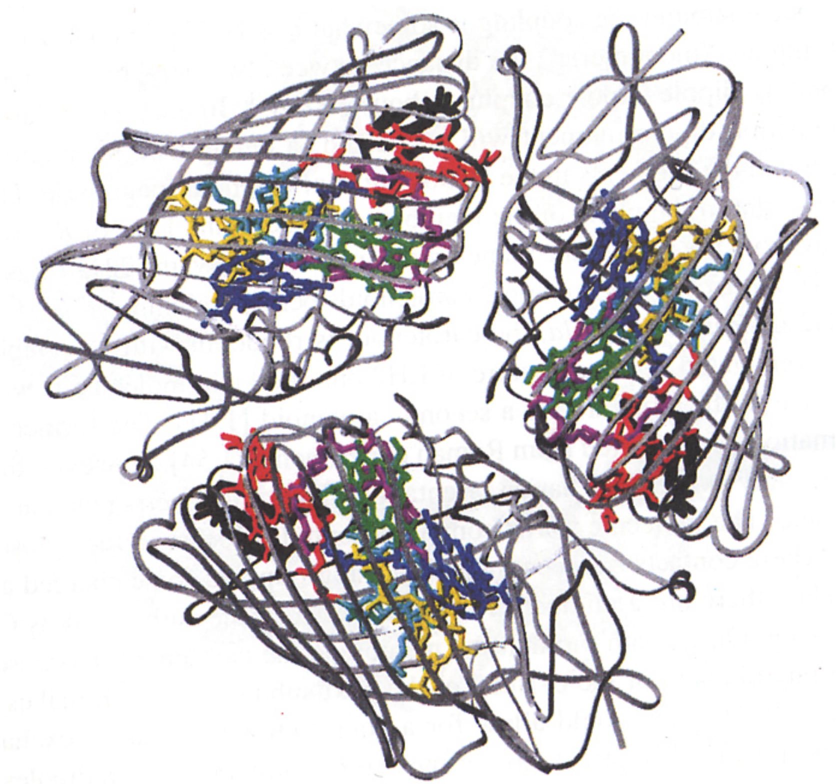
Biology of *C. tep* & FMO

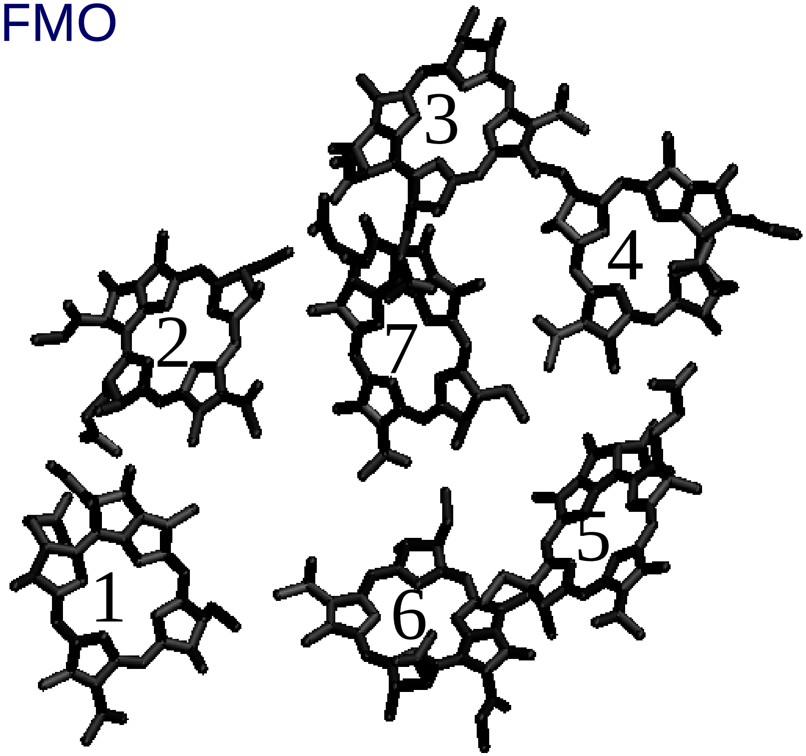
- FMO's role in light harvesting
  - Trimer structure
  - Monomer contains seven chlorophylls
  - Energetic wire connecting chlorosome to Reaction center



Trimeric FMO complex

- ➢Closely packed BChls in hydrophobic protein environment
- ➢BChls in different subunits are very far apart – only need to consider the 7 BChls in a monomer of FMO





Spatial arrangement of BChls

How does the excitation energy move in space through the complex?
How do Layout, Couplings, and Energy Conspire?

Role of Coherence in Photosynthetic Light-Harvesting

1. How do you observe it?
2. How do you model it?
3. What good is it?
4. What causes the coherence to decay?
5. What about the role of molecular vibrations?
6. What do we mean by energy transfer?
7. Are there new experiments that would help?
8. But isn't the sun an incoherent light source?

How do you observe it?

Quantum Superposition States Oscillate with Frequency Equal to Energy Difference between Energy Levels

$$|\Psi(t)\rangle = a e^{-i\omega_1 t}\,|e_1\rangle + b e^{-i\omega_2 t}\,|e_2\rangle$$

- Evolution of quantum superpositio

population

- Density matrix

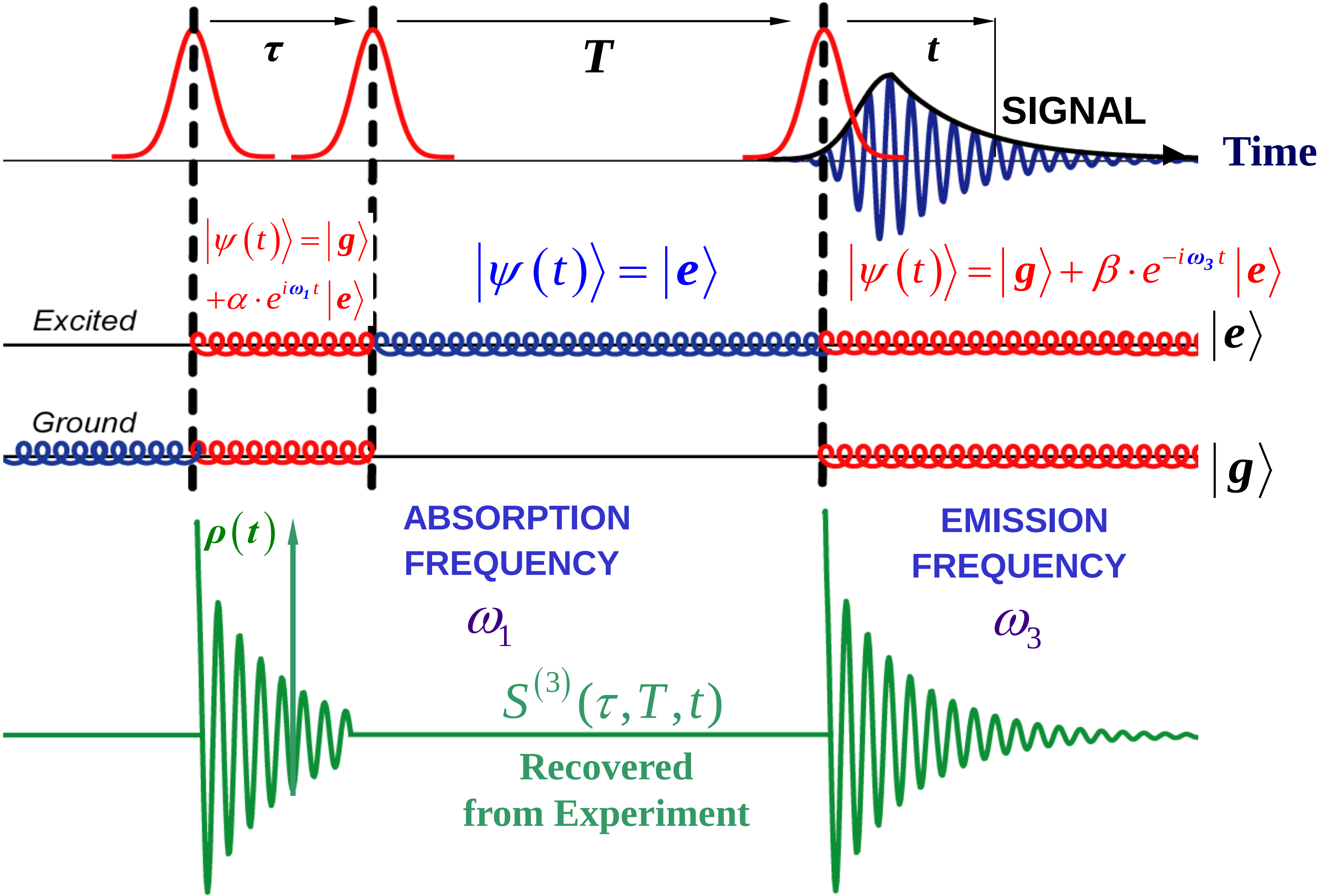
$$|\Psi(t)\rangle\langle\Psi(t)| \;=\; \boxed{a\,|e_1\rangle\langle e_1| + b\,|e_2\rangle\langle e_2|}$$

$$\boxed{+ab^{*}e^{-i(\omega_1-\omega_2)t}\,|e_1\rangle\langle e_2| + a^{*}b e^{i(\omega_1-\omega_2)t}\,|e_2\rangle\langle e_1|}$$

- 2D electronic spectroscopy can measure the phase evolution of coherences.

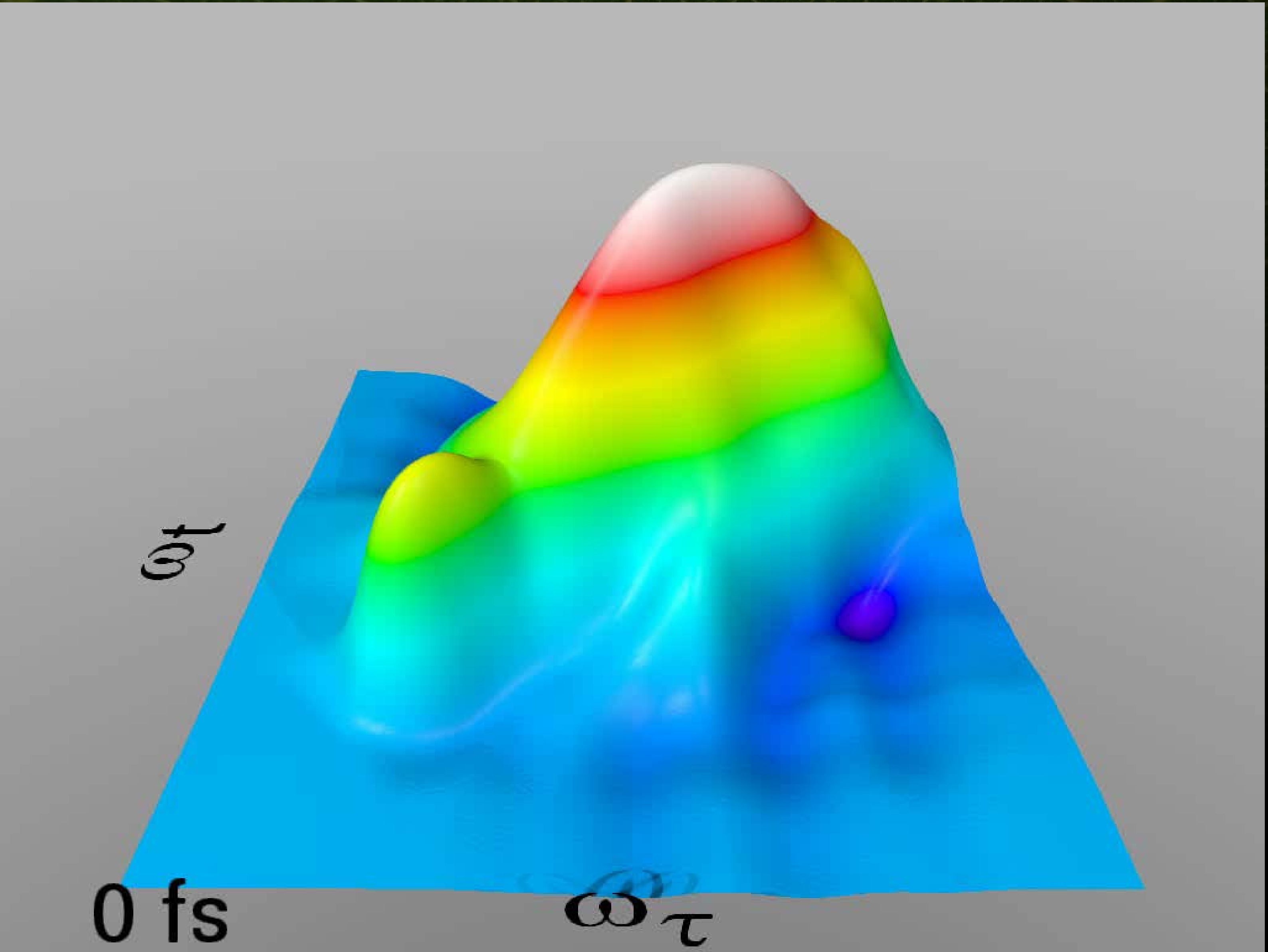
coherence

Principles of 2D Spectroscopy



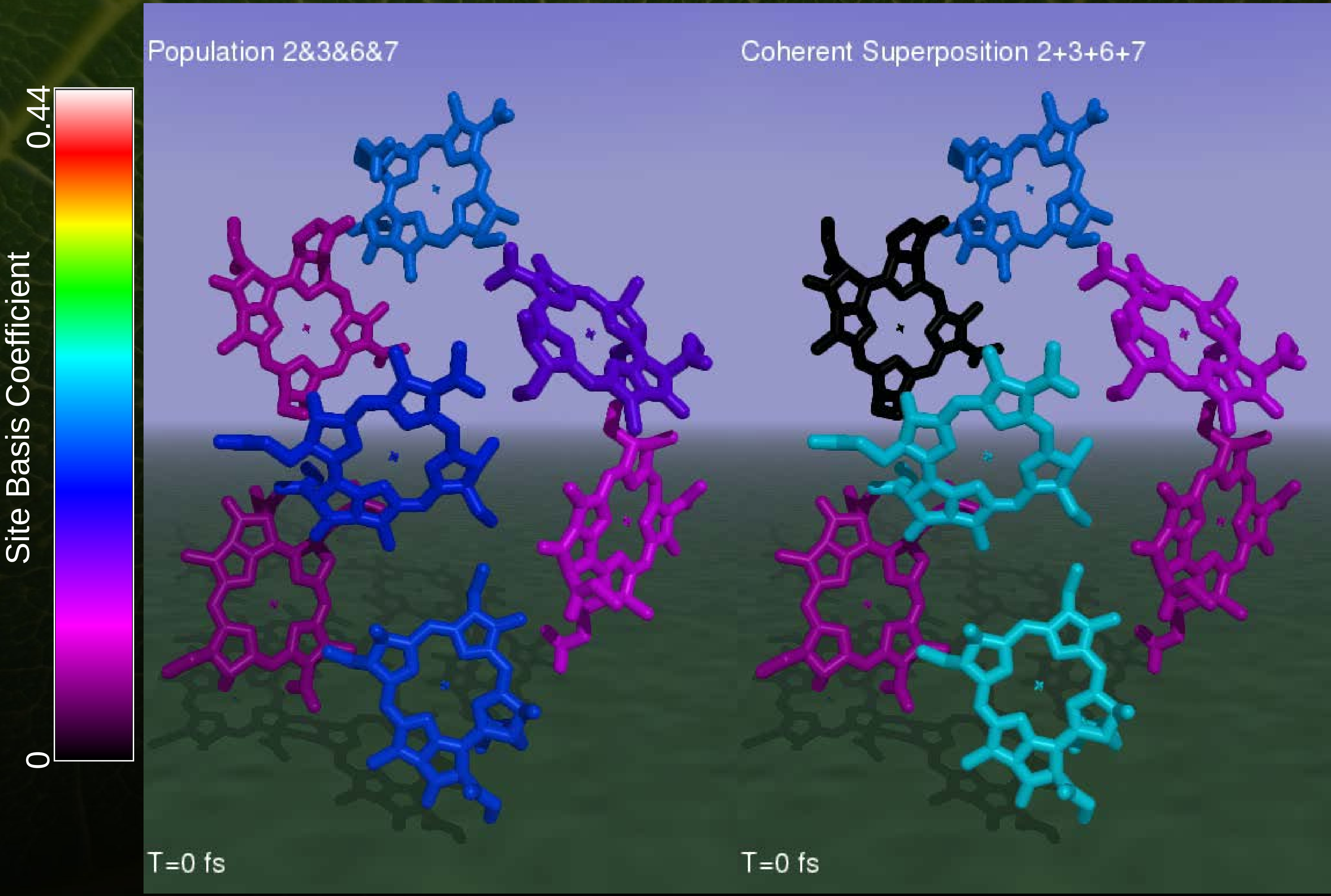
- ➢ Obtain $S^{(3)}(w_1,T,w_3)$ by double Fourier Transformations in τ and t
- ➢ Retrieves Correlation between Absorption and Emission Frequencies

C. tep FMO Data

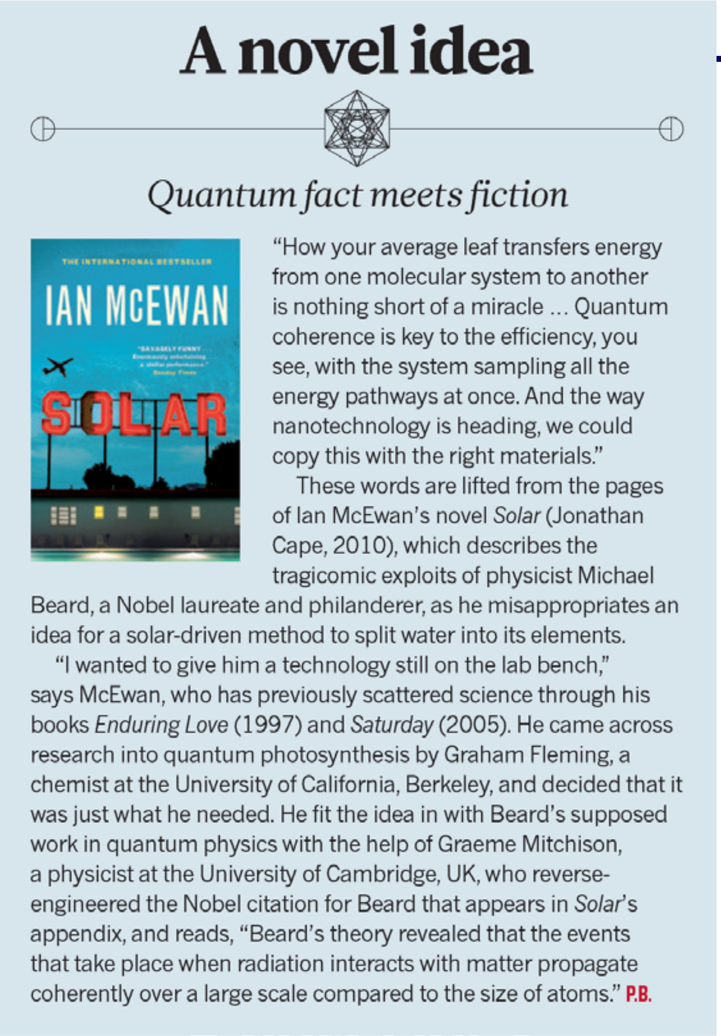


Measured Points:

0, 10, 20, 30, 40, 50, 65, 80, 95, 110, 125, 140, 155, 170, 185, 200, 220, 240, 260, 280, 300, 330, 360, 390, 420, 450, 480, 510, 540, 570, 600, 630, 660fs


Site Basis Coefficient
0.44
0
Population 2&3&6&7
Coherent Superposition 2+3+6+7
T=0 fs
T=0 fs

The dawn of quantum biology



A novel idea

Quantum fact meets fiction

"How your average leaf transfers energy from one molecular system to another is nothing short of a miracle … Quantum coherence is key to the efficiency, you see, with the system sampling all the energy pathways at once. And the way nanotechnology is heading, we could copy this with the right materials."

These words are lifted from the pages of Ian McEwan's novel *Solar* (Jonathan Cape, 2010), which describes the tragicomic exploits of physicist Michael Beard, a Nobel laureate and philanderer, as he misappropriates an idea for a solar-driven method to split water into its elements.

"I wanted to give him a technology still on the lab bench," says McEwan, who has previously scattered science through his books *Enduring Love* (1997) and *Saturday* (2005). He came across research into quantum photosynthesis by Graham Fleming, a chemist at the University of California, Berkeley, and decided that it was just what he needed. He fit the idea in with Beard's supposed work in quantum physics with the help of Graeme Mitchison, a physicist at the University of Cambridge, UK, who reverse-engineered the Nobel citation for Beard that appears in *Solar*'s appendix, and reads, "Beard's theory revealed that the events that take place when radiation interacts with matter propagate coherently over a large scale compared to the size of atoms." P.B.

Phillip Ball
Nature, July 2011

The View from Cambridge, Massachusetts

One morning in the Spring of 2007, I read in the New York Times that green sulphur bacteria were performing quantum computation,
I thought it must be some kind of crackpot idea.

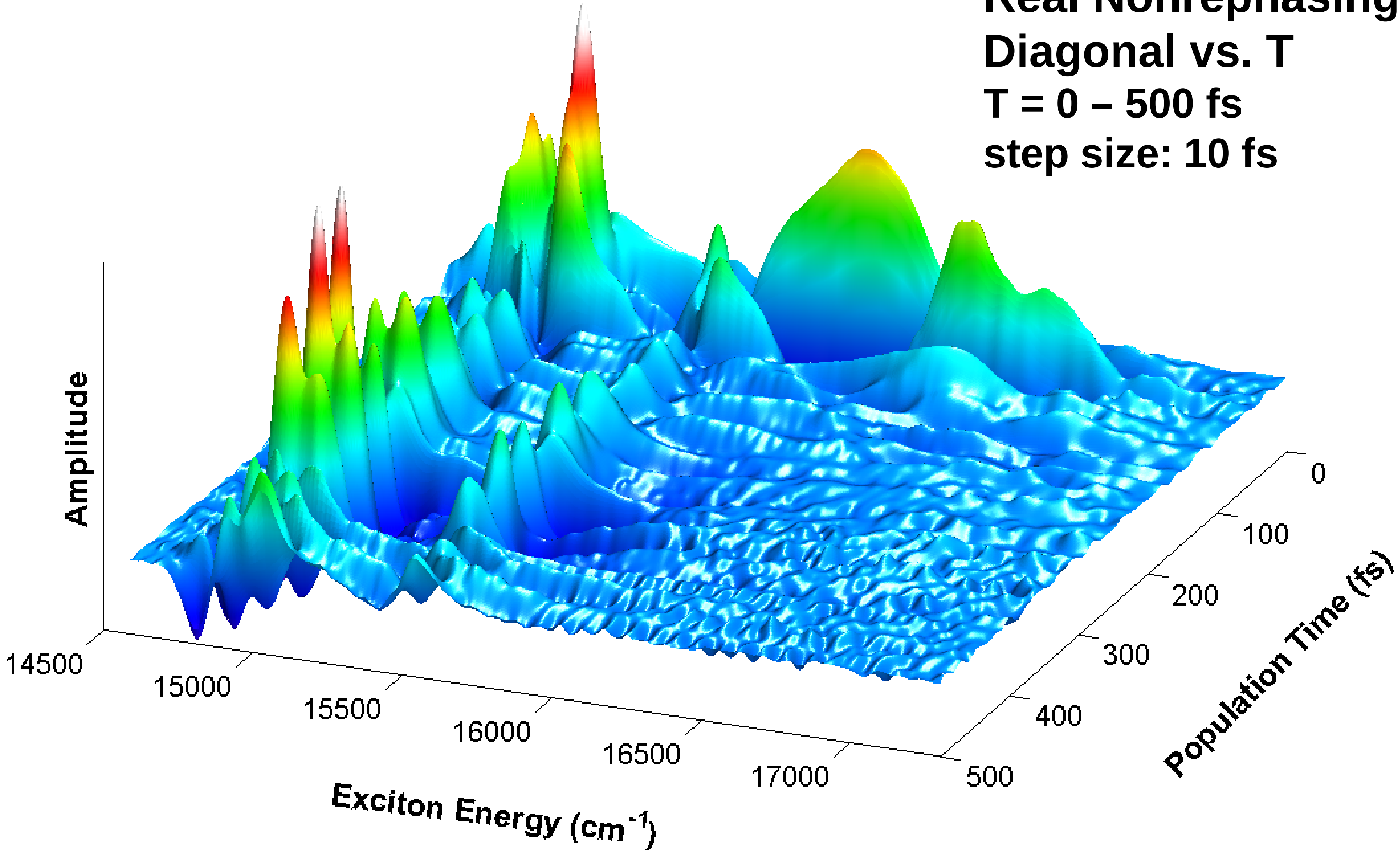
Later that day, the quantum computing group at MIT held its weekly meeting at which everyone present had a good laugh at the notion of bacteria using quantum coherence and entanglement to assemble chemical energy from sunlight.

When I looked at the Nature paper on which the NYT article was based, I found it was written not by crackpots but by a well-known group of researchers at Berkeley, led by the eminent spectroscopist Graham Fleming.

--The evidence for quantum coherence in the way that the bacteria transported energy was impeccable.

Seth Lloyd
Physics World, January 2011

LHCII Coherence

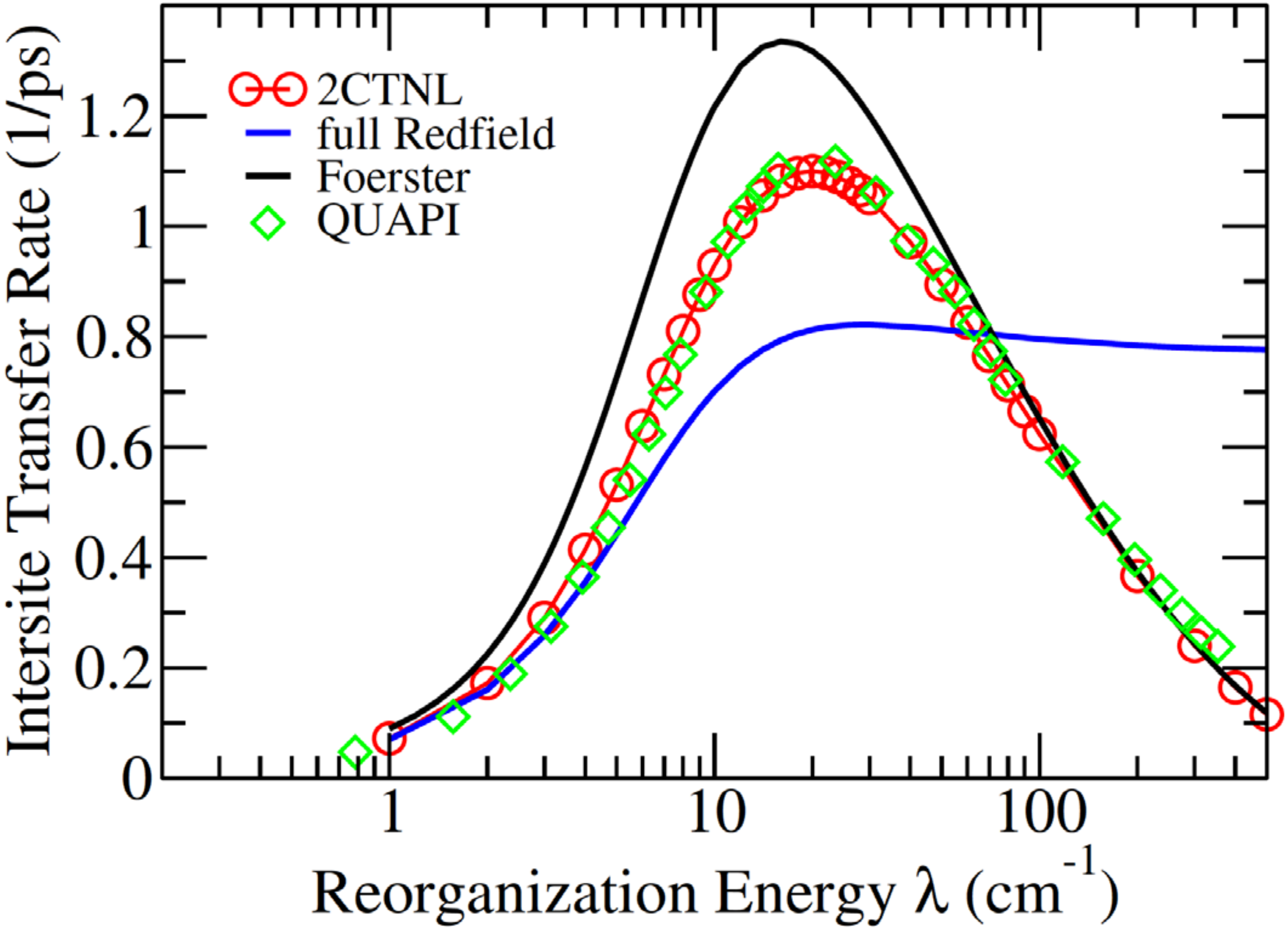


Real Nonrephasing
Diagonal vs. T
T = 0 – 500 fs
step size: 10 fs

How do you model it?

Calculating Energy Transfer Rates

Path Integral Method (QUAPI) vs. Time-nonlocal Quantum Master Equations (2CTNL)



Relevant Regime:

$\lambda \sim J \sim 1/\tau_c$

λ = reorganization energy

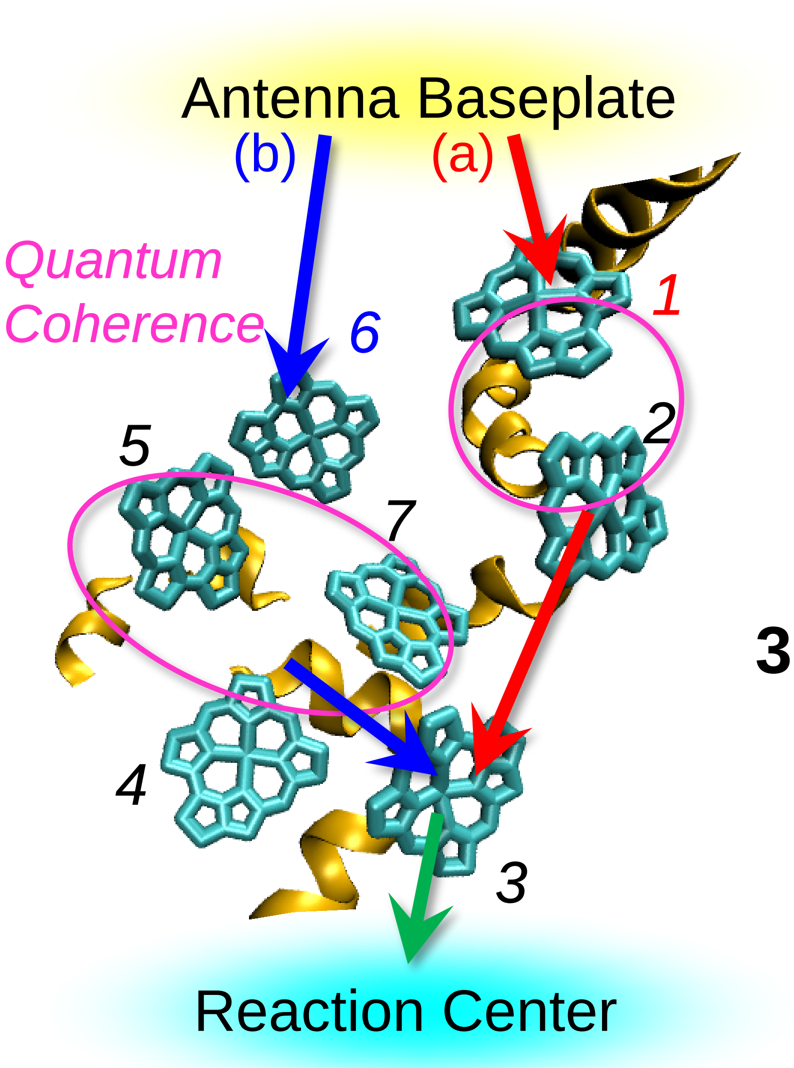
J = electronic coupling

τ_c = environment relaxation time

Non-Markovian correlations and fluctuations are correctly incorporated

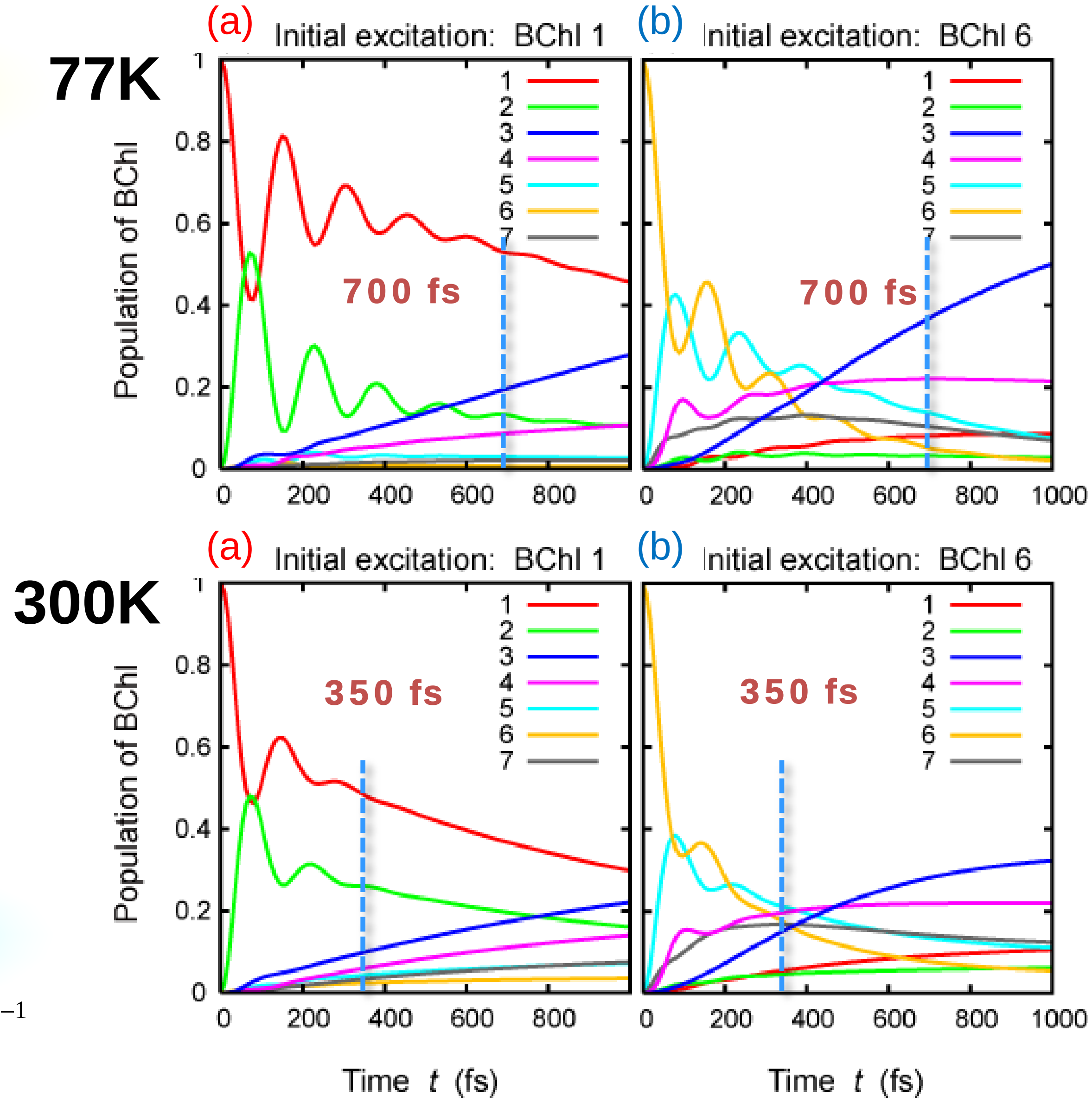
Ishizaki and Fleming, J. Chem. Phys. 130, 234111 (2009)
Nalbach, Ishizaki, Fleming, Thorwart, New J. Phys. 13, 063040

Coherent Energy Transfer through the FMO Complex



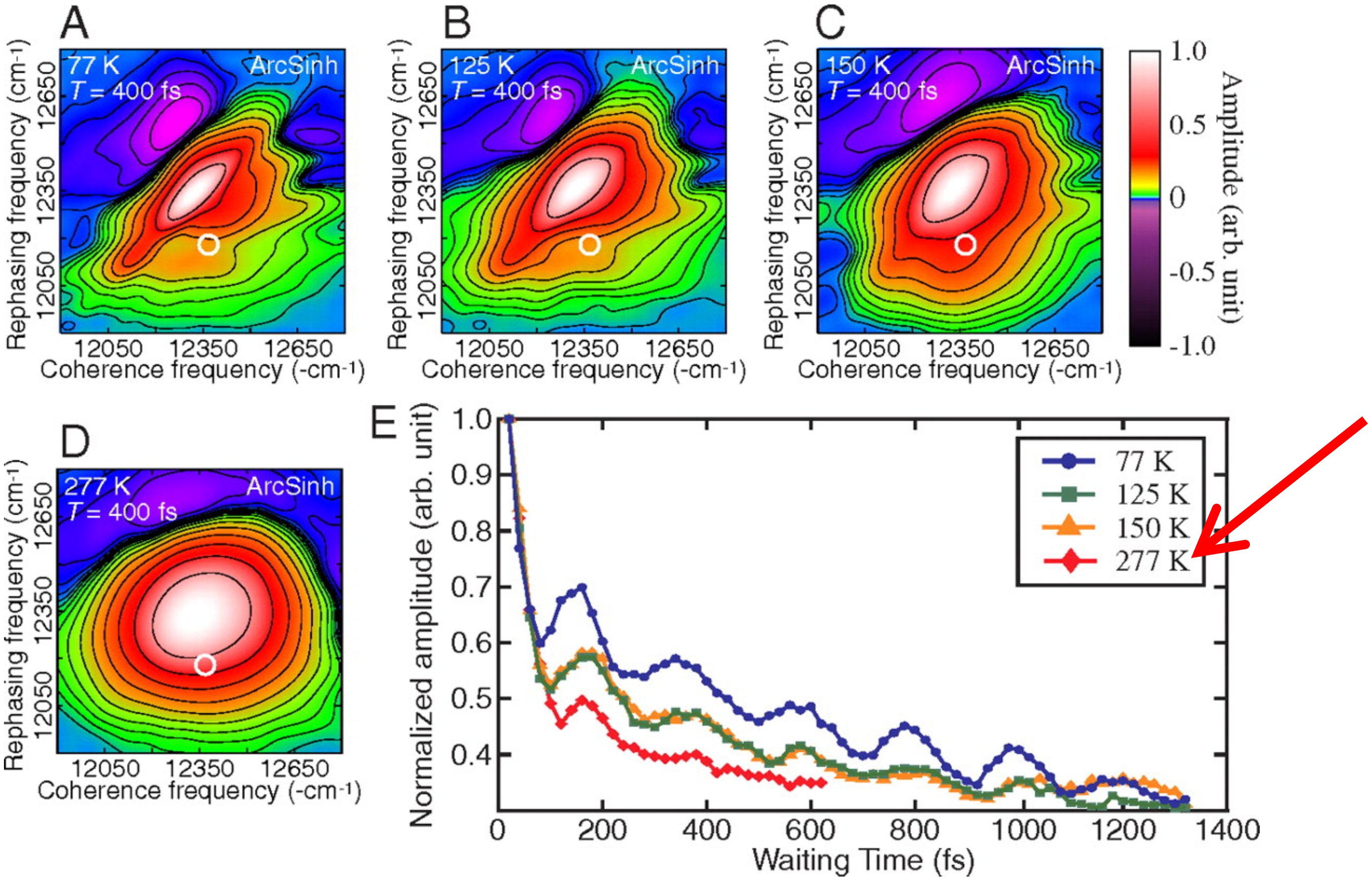
Reorganization energy : $\lambda = 35\,\mathrm{cm}^{-1}$

Phonon relaxation time: $\tau = 50\,\mathrm{fs}$



Coherence Decay in FMO (Engel and coworkers)

Experimental Results



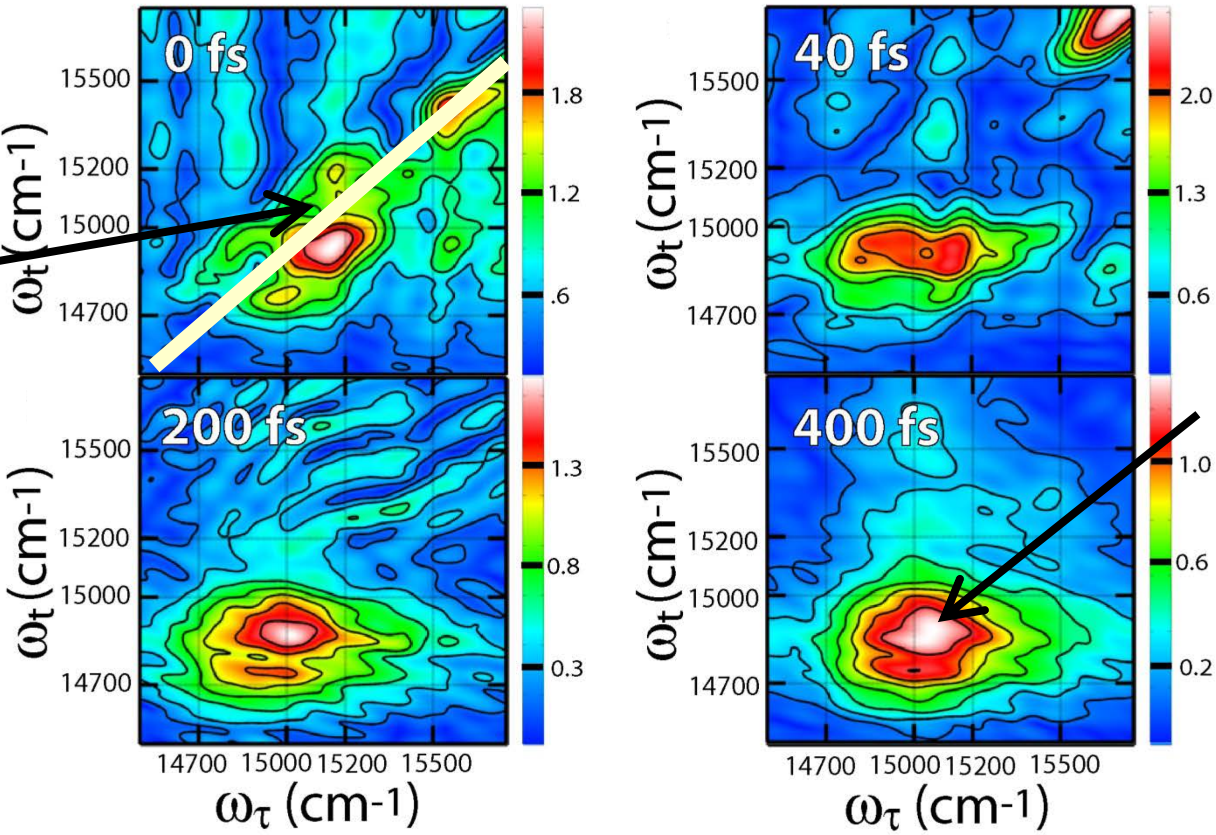
Theory predicted oscillatory behavior lasts ~350 fs

Panitchayangkoon G et al. PNAS 2010;107:12766-12770

Spectra provide means to observe only signals from electronic coherence

Polarized, absolute value, non-rephasing spectra

(π/4,–π/4,π/2,0)

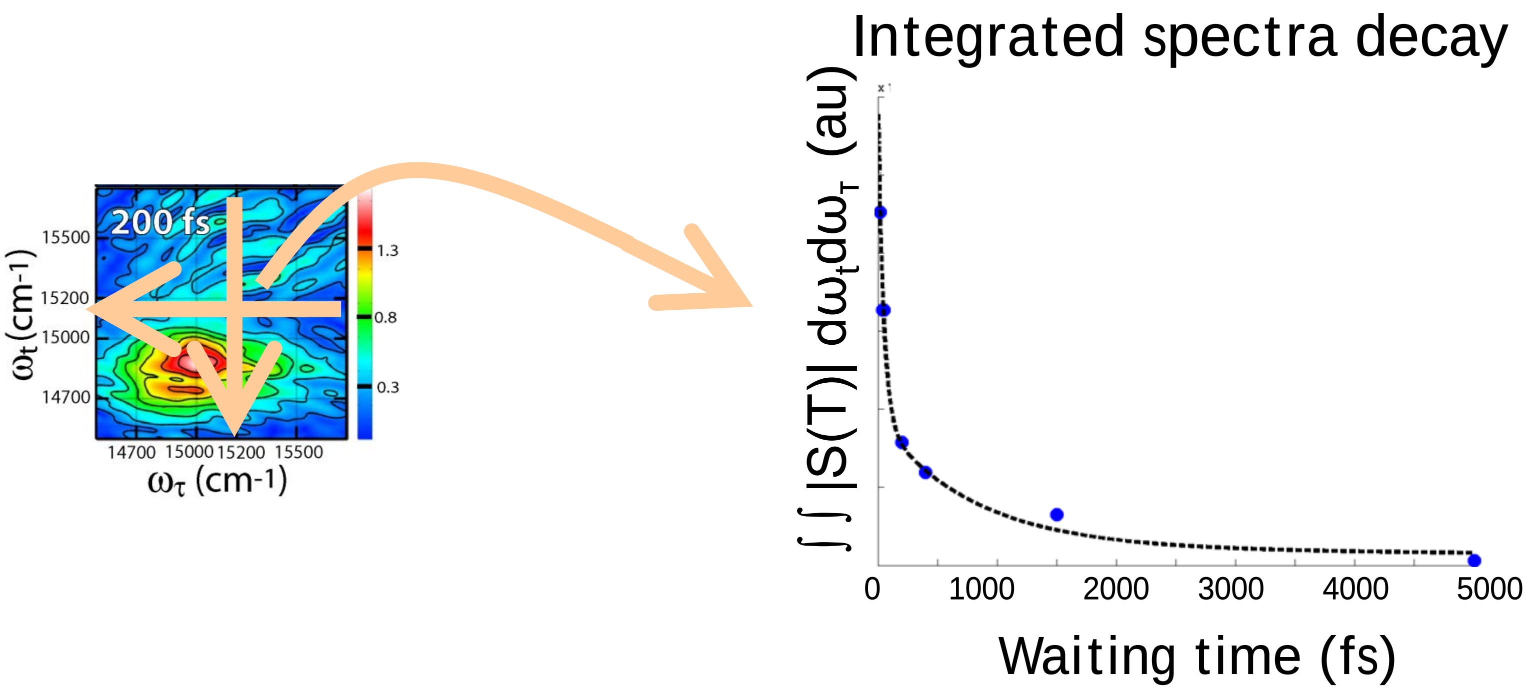


Diagonal peaks show coherence in all regions

Mid energy Chl-a peak exhibits particularly strong coherence signal

Timescale of coherence indicates contribution of coherence to energy transfer & reflects strength of Chl-Chl coupling

How long can we observe coherence in LHCII?



Decay components

Short time decay	46.5 fs	From parallel data
Excitonic decoherence ($\lvert e_i\rangle\langle e_j\rvert$ decoherence)	**795 fs**	**From polarized data**
Decay of overall signal	13.74 ps	From parallel data

From integrated signal lifetime, coherence dephasing time of system at 77 K extracted: ~700-900 fs

What Determines the Lifetime of Intra-excitonic Coherence?

After all we know that $\langle g|e\rangle$ coherences decay very rapidly

Adiabatic Picture

The electronic coupling lowers the barrier between the two sites allows oscillatory motion above the barrier until environmental relaxation localizes the excitation in one well:

$$(\mathrm{J} \sim \Delta \mathrm{E} \sim \quad \lambda \quad \tau_{rel}^{-1})$$

Energy Gap Fluctuation Picture

For two excitons $|e_a\rangle$ and $|e_b\rangle$ the fluctuation of the energy gap between them will destroy the coherence.

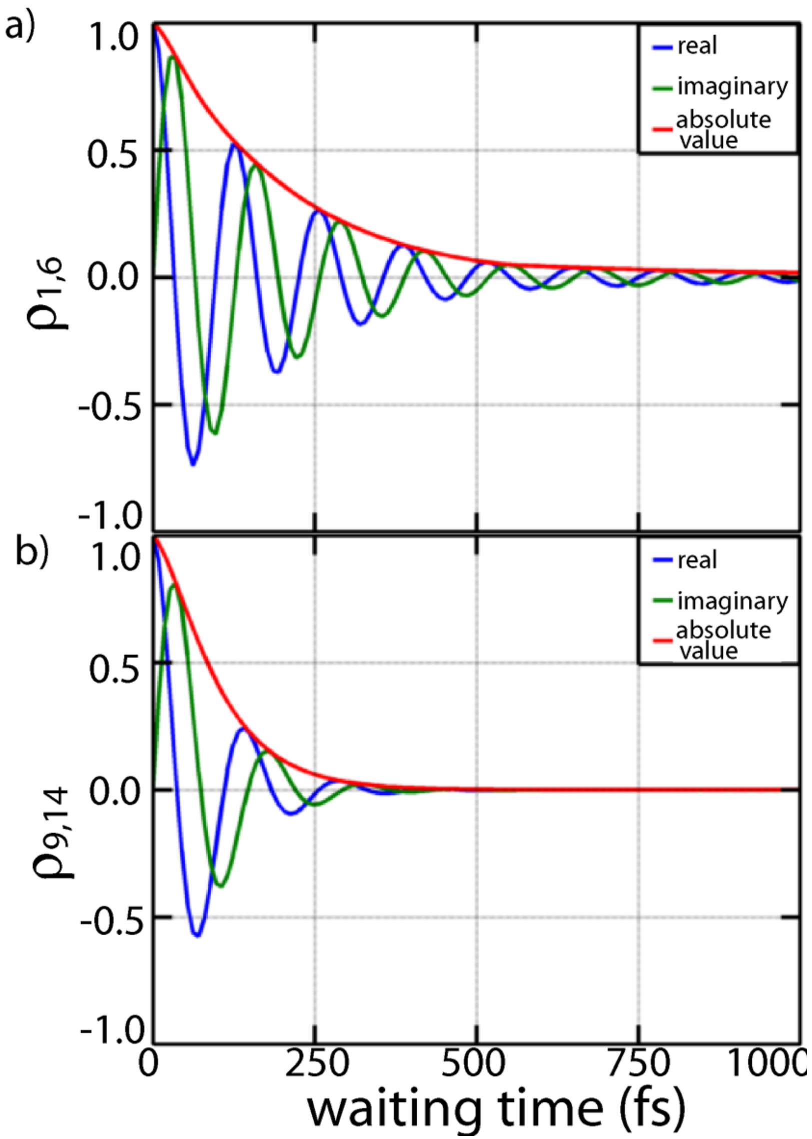
If $|e_a\rangle$ and $|e_b\rangle$ share the same pigments (have spatial overlap)

$$C_b^a(t) = \langle \delta E_a(t) \delta E_b(0) \rangle \neq 0$$

and the dephasing is given by: $S_{ab}(t) = C_{aa}(t) + C_{bb}(t) - C_{ab}(t) - C_{ba}(t)$

Thus as J_{12} increases the rms fluctuation amplitude decreases

Two timescales correspond to strongly & weakly coupled chlorophyll



Wavelike motion of the excitation in the site basis, or coherent energy transfer, arises from strong electronic coupling

Weak coupling leads to time-independent probabilities of the observing the excitation on the individual sites

What good is it it?

Uses of Coherence in Light-Harvesting

Achieve fastest rate: Balance of coherent and incoherent energy transfer

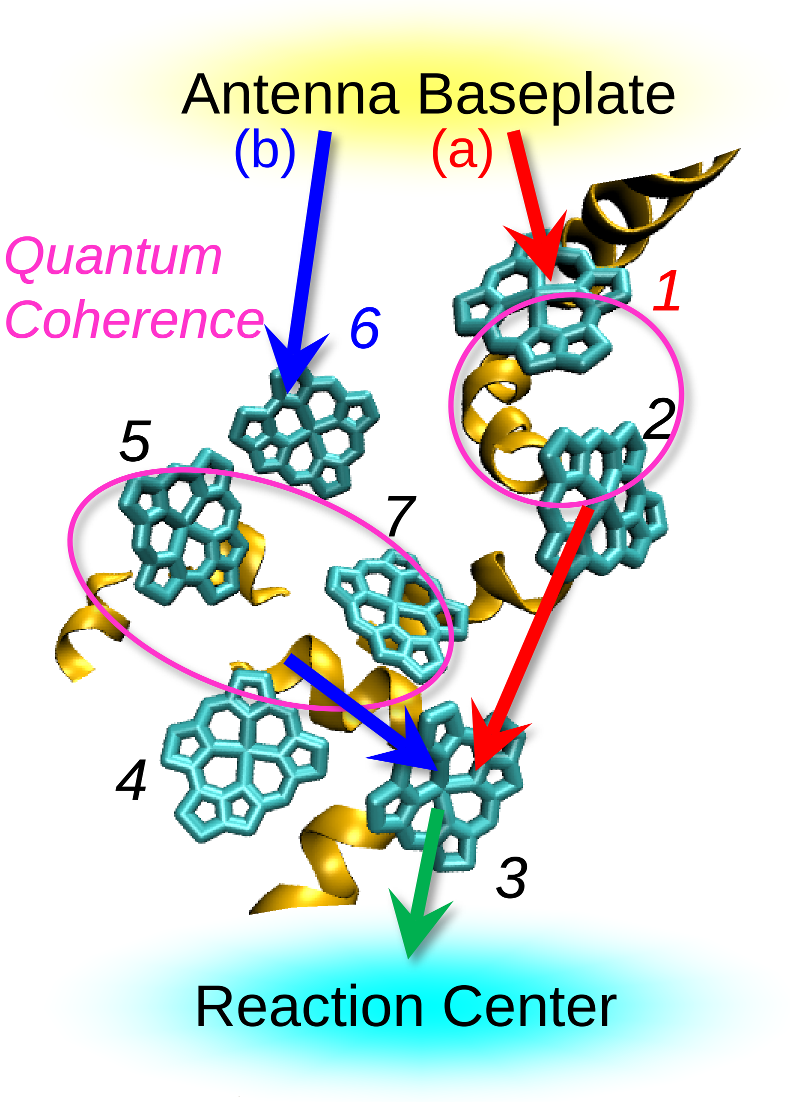
Uni-directionality: Manipulating rate constants, which affects forward vs. backward flow

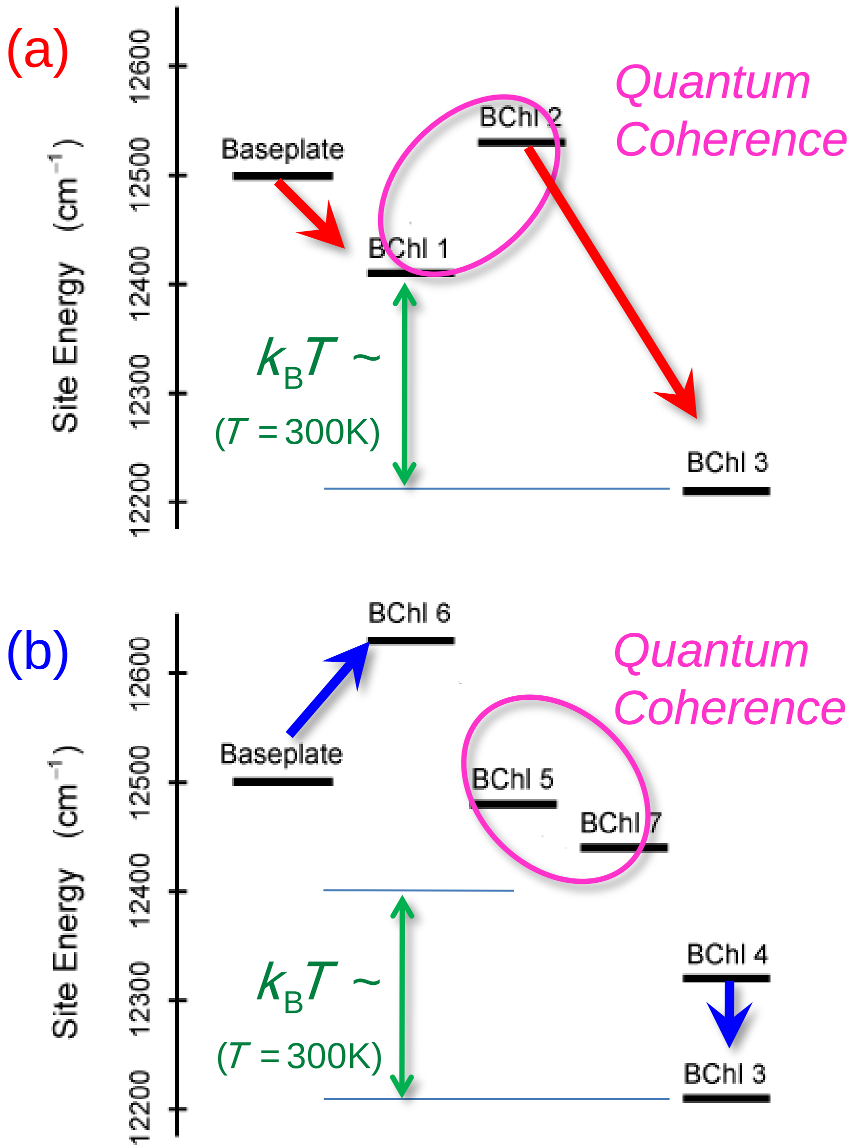
Robust to trap states: Avoid lower energy traps in rough energy landscape; reorganization energy implies potential for trapping

Interference of energy transfer pathways: Multiple pathways produces constructive and destructive interference

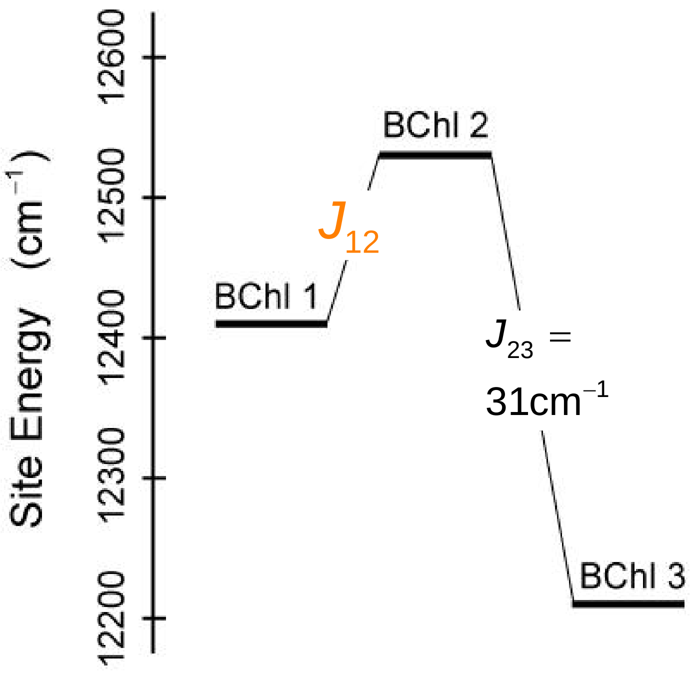
Temperature insensitivity: Transfer rates ~independent of temperature

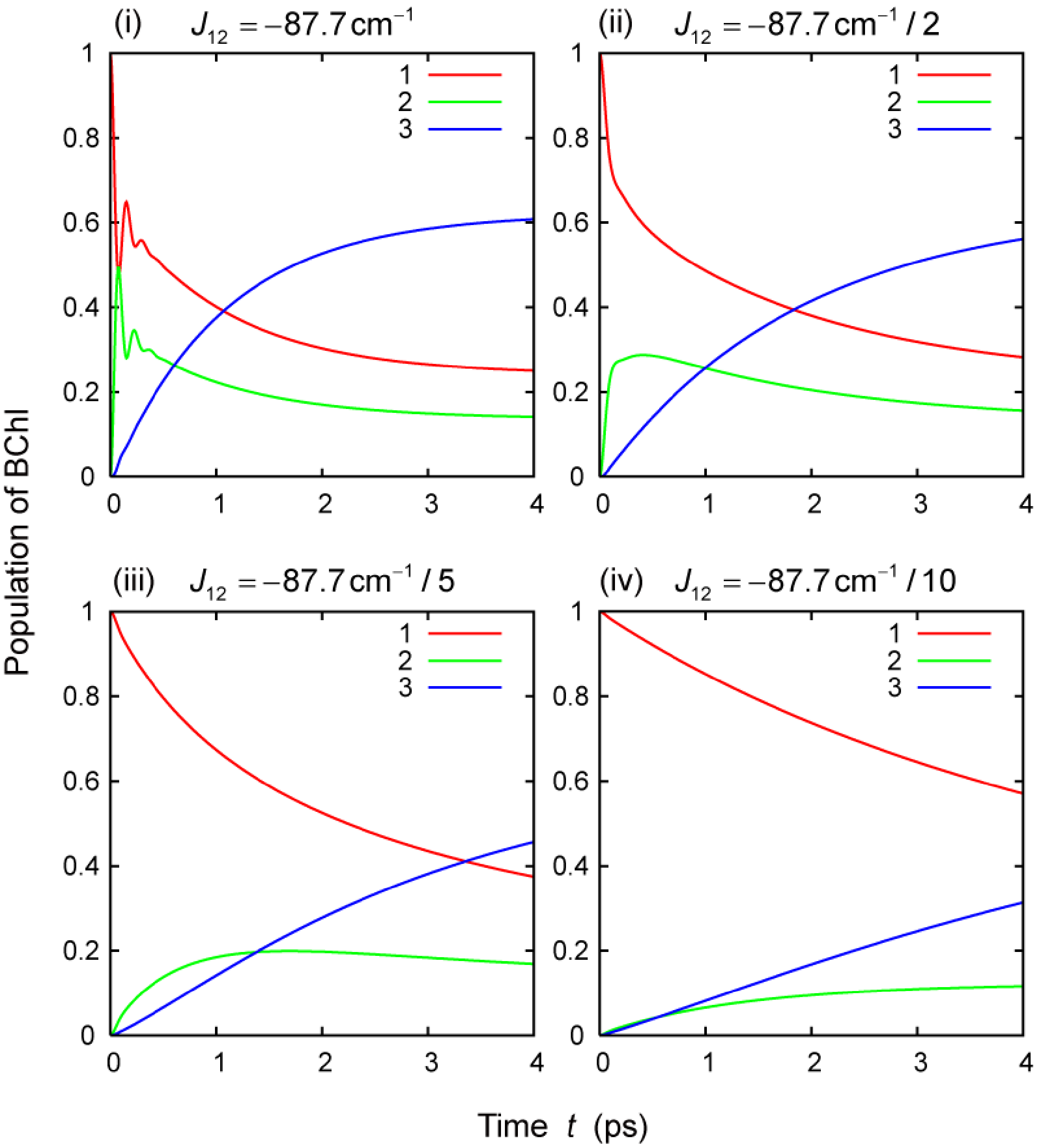
Energy Landscapes along Two Primary Pathways





Influence of Coherence between BChls 1 and 2





Temperature: $T = 300\,\mathrm{K}$

Reorganization energy: $\lambda_j = 35\,\mathrm{cm}^{-1}$

Protein relaxation time: $\tau_j = 50\,\mathrm{fs}$

What causes the coherence to decay?

Decoherence (1)

‘Real’ vs ‘Fake’

Loss of ‘Quantum Mechanicalness’ of system

***Apparent* loss of ‘Quantum Mechanicalness’ of system**

- **‘Real’ decoherence** is a quantum mechanical effect with no classical analog. It leads to an entangled state for the combined system and environment when both are treated quantum mechanically: $|\psi^{\mathrm{tot}}(t)\rangle = \sum_n c_n(t)|\varphi_n^{\mathrm{sys}}\rangle|\theta_n^{\mathrm{env}}(t)\rangle$.

- When measurements are done on the system, a portion of the information on the system is lost.

- If we trace over the inaccessible environmental state, we obtain as the reduced density matrix of the entangled subsystem as:

$$\rho_{\mathrm{reduced}}(t) = \sum_{mn} c_m(t)c_n^*(t)\langle\theta_m^{\mathrm{env}}(t)|\theta_n^{\mathrm{env}}(t)\rangle \cdot |\varphi_m^{\mathrm{sys}}\rangle\langle\varphi_n^{\mathrm{sys}}|$$

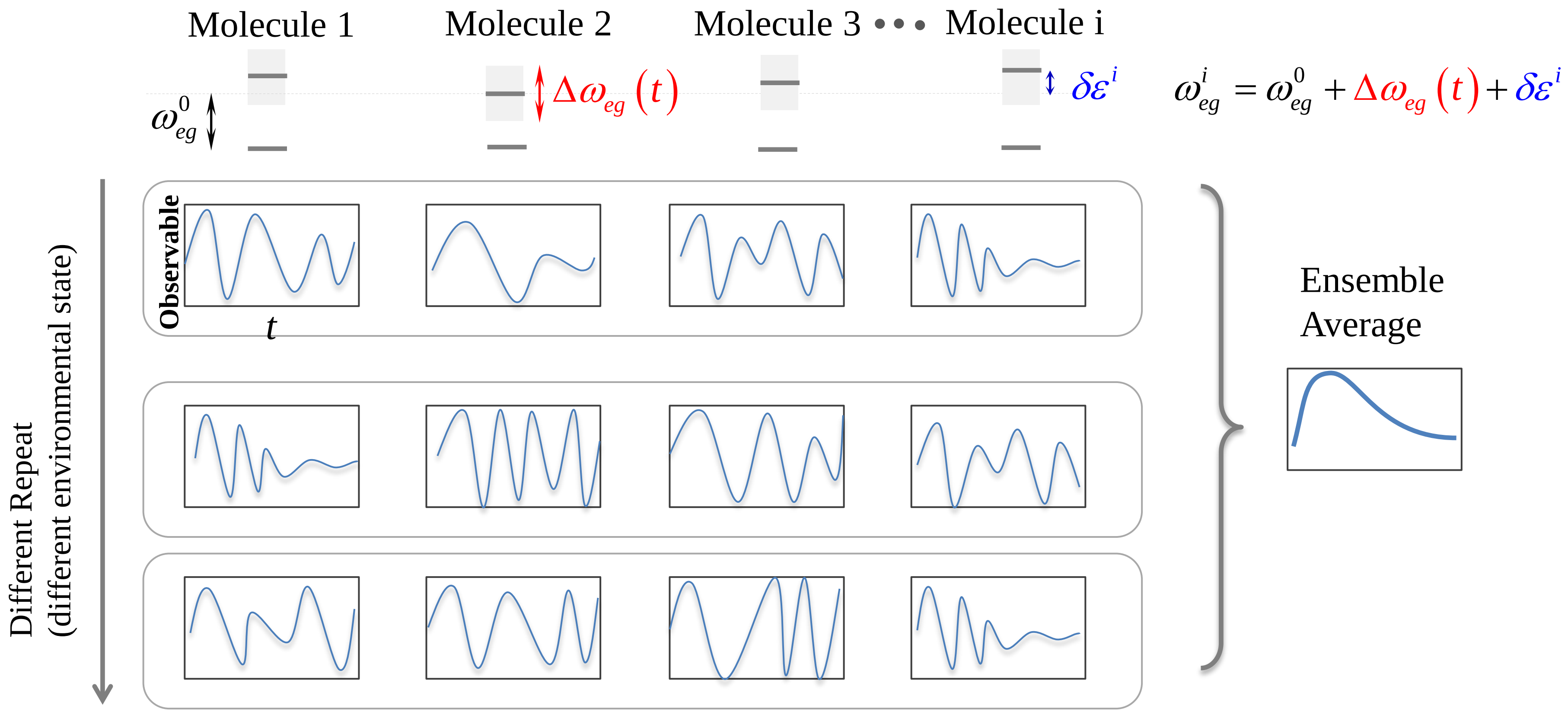
- Over time the overlaps between the environmental states $|\theta_m^{\mathrm{env}}(t)\rangle$ with the system state, , $|\varphi_m^{\mathrm{sys}}\rangle$ become small. Thus the $\{|\theta_n^{\mathrm{env}}(t)\rangle\}$ become mutually orthogonal,

$$\langle\theta_m^{\mathrm{env}}(t)|\theta_n^{\mathrm{env}}(t)\rangle \longrightarrow \delta_{mn}$$

and the off-diagonal terms in $\rho_{\mathrm{reduced}}(t)$ disappear.

M. A. Schlosshauer, "Decoherence and the Quantum-to-Classical Transition" Springer, Berlin (2007).

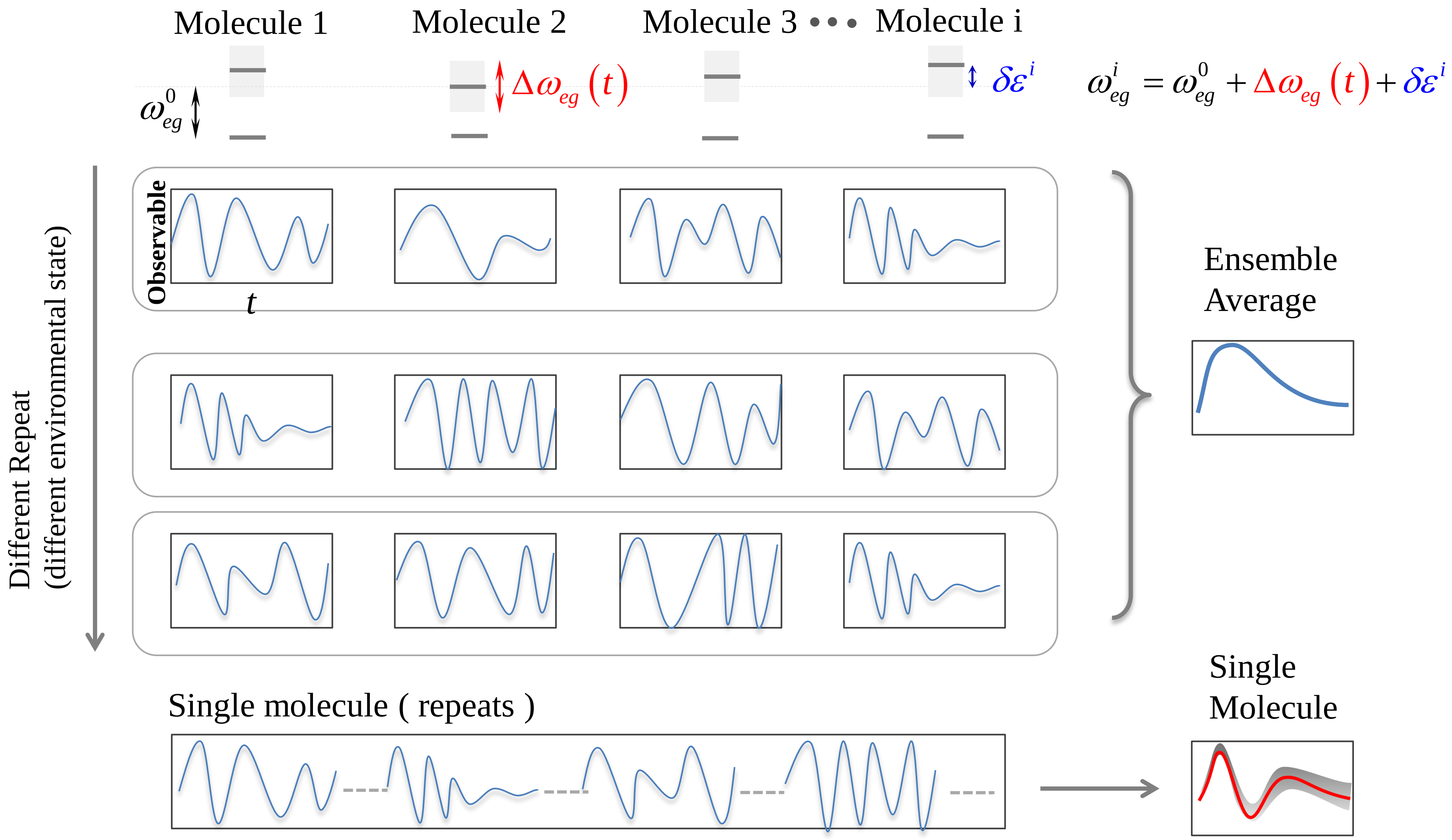
Ensemble vs Single Molecule



$$\omega_{eg}^{i} = \omega_{eg}^{0} + \Delta\omega_{eg}(t) + \delta\varepsilon^{i}$$

A. Ishizaki and **GRF**, J. Phys. Chem. B 115, 6227(2011)
J. M. Dawlaty, A. Ishizaki, A.K.De, and **GRF**, Philos T R Soc A, 370 , 3672 (2012)

Ensemble vs Single Molecule



Molecule 1 Molecule 2 Molecule 3 • • • Molecule i

ω_{eg}^{0} $\Delta\omega_{eg}(t)$ $\delta\varepsilon^{i}$

$$\omega_{eg}^{i} = \omega_{eg}^{0} + \Delta\omega_{eg}(t) + \delta\varepsilon^{i}$$

Observable

t

Different Repeat
(different environmental state)

Ensemble
Average

Single molecule (repeats)

Single
Molecule

A. Ishizaki and **GRF**, J. Phys. Chem. B 115, 6227(2011)

J. M. Dawlaty, A. Ishizaki, A.K.De, and **GRF**, Philos T R Soc A, 370 , 3672 (2012)

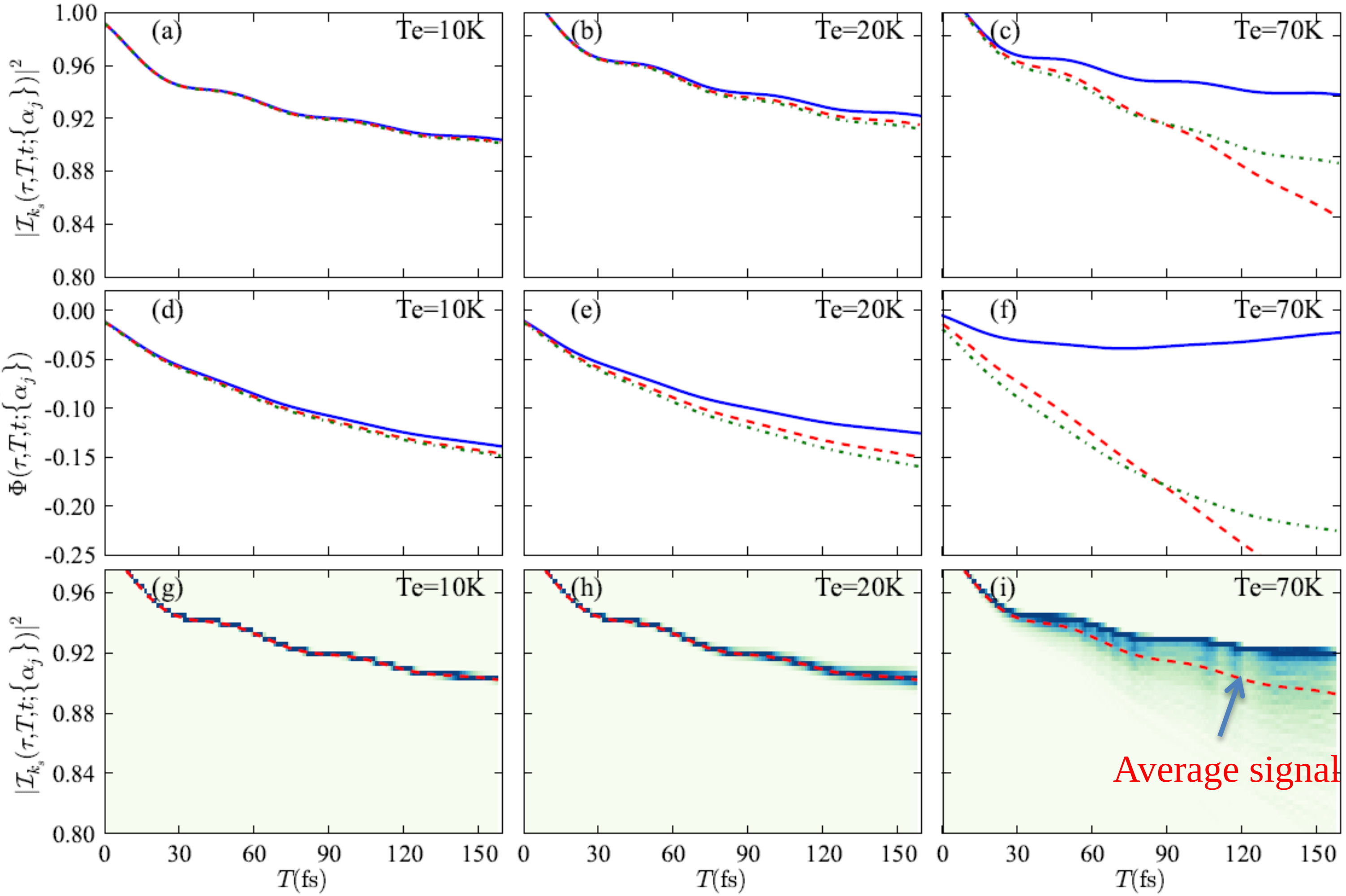
Three-Pulse Photon Echo Traces & Distribution

$t = \tau = 10\text{fs}$ λ=$100cm^{-1}$ ω_c=$100cm^{-1}$

Signals with different $\{\alpha_j\}$

Random phase with different $\{\alpha_j\}$

Overall distribution



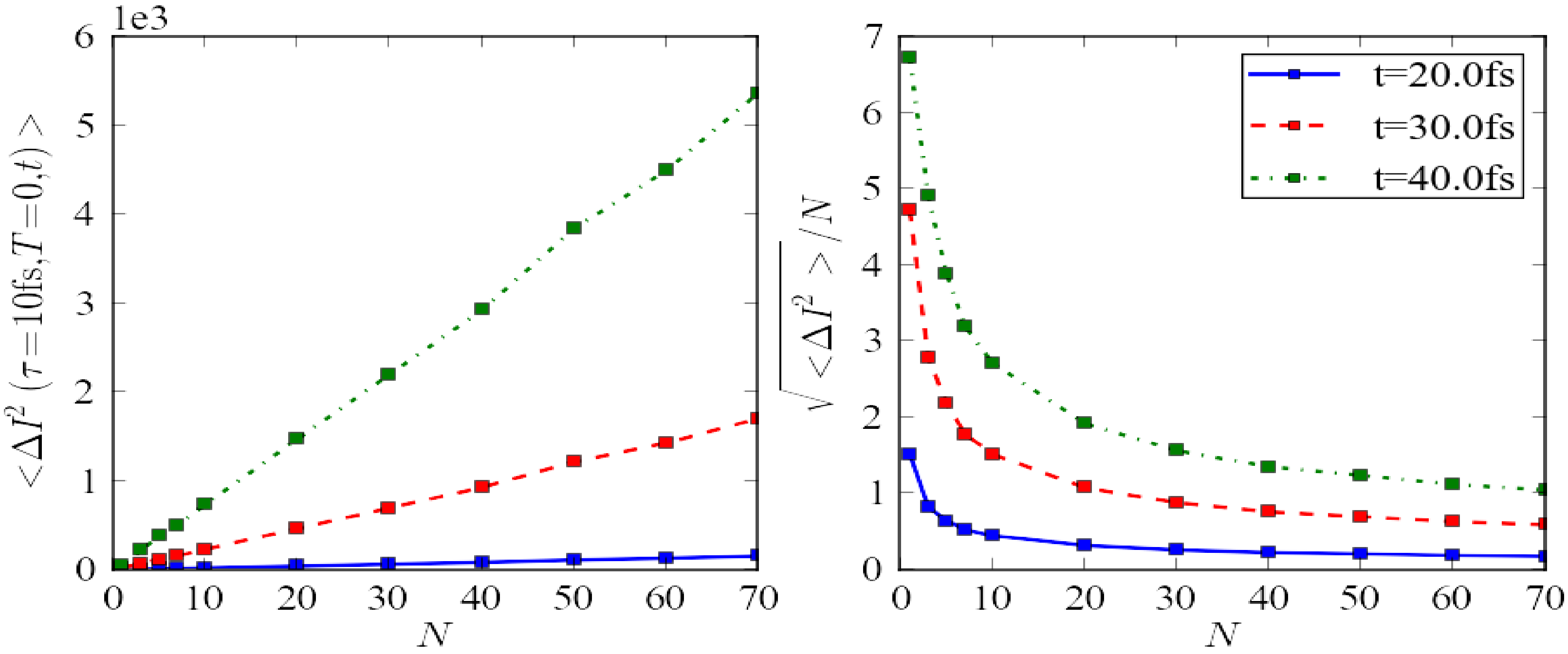
Average signal

H.Dong and **GRF**, (2013) JPC B in press

Fluctuation & Number of Molecules

Fluctuation of the photon-echo signal

$$\left\langle \Delta I^2(t) \right\rangle = <(I(t) - <I>)^2> \propto N \qquad \sqrt{\left\langle \Delta I^2(t) \right\rangle} / N \propto 1/\sqrt{N}$$

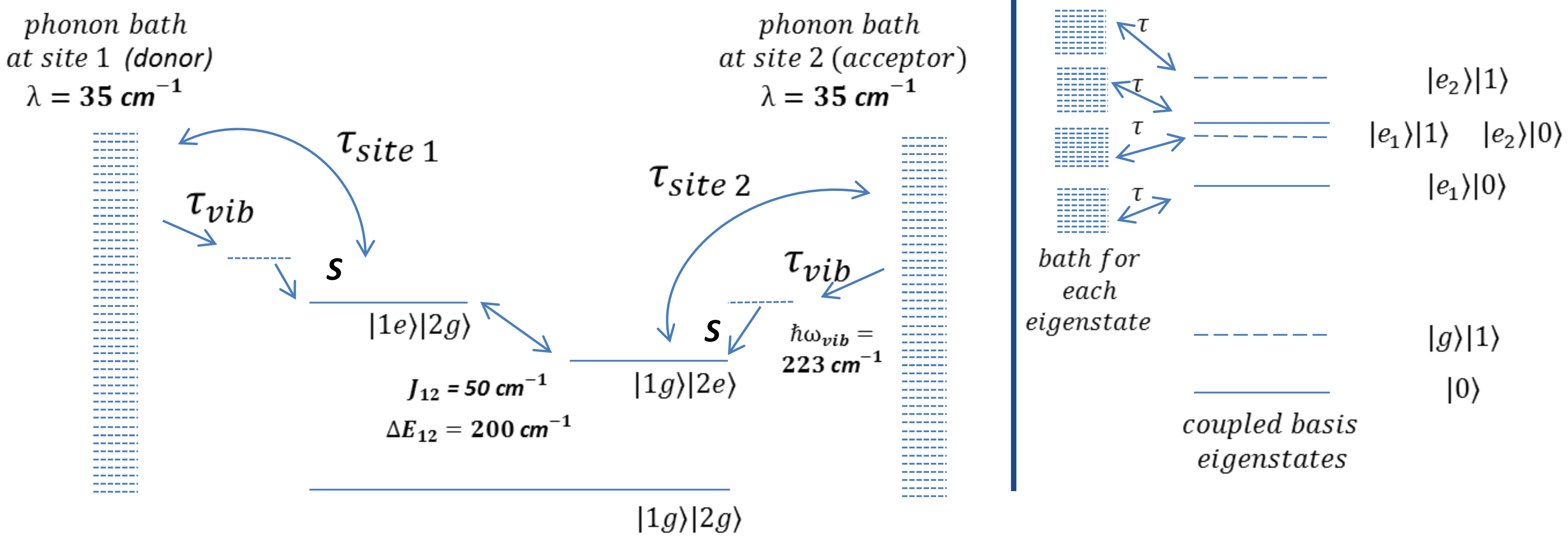


What about the role of molecular vibrations?

Electronically Excited Dimer Coupled to Bath and Vibration: A Numerically Accurate Approach

Site Basis Picture

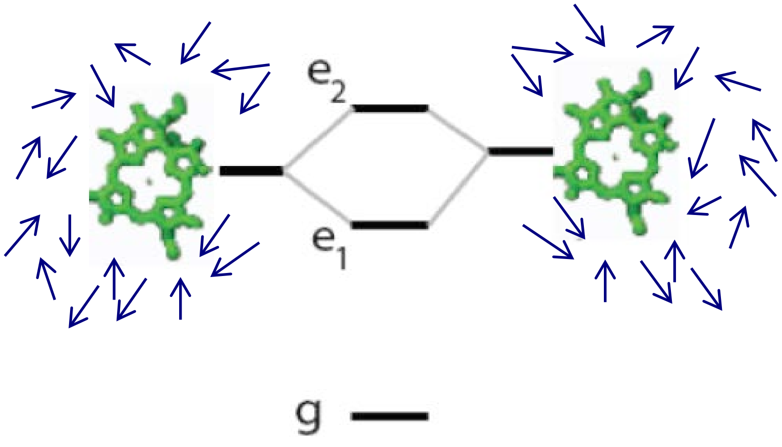
…vs Exciton Basis Picture

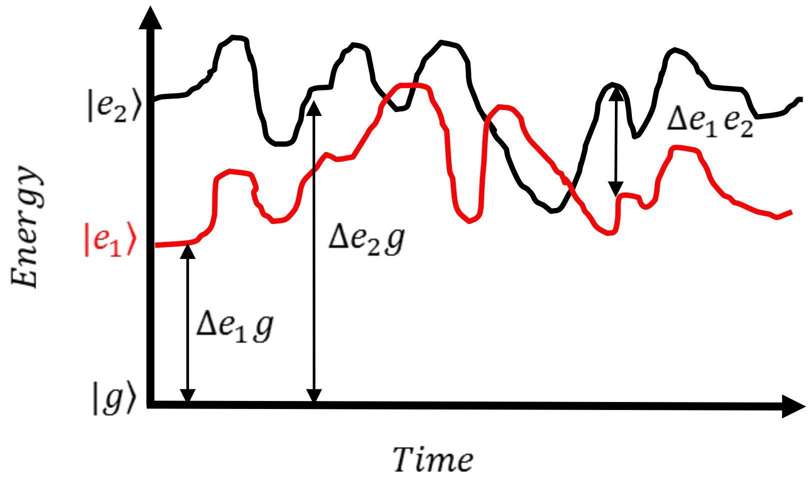


- Each site is dissipated by an identical phonon bath and a selected vibration, e.g. a strongly coupled intramolecular mode;
- The vibration is itself damped by the bath with $\tau_{vib} \gg \tau_{site\ j}$.

Akihito Ishizaki

Why propagate dynamics in the site basis?





- In the intermediate coupling regime, $H_{\text{el-ph}}$ depends largely on bath degrees of freedom, so $H_{\text{ex}} + H_{\text{el-ph}}$ has no static energy eigenstates.
- System-bath interactions (e.g. phonon scattering) are site dependent and thus *distinguish between sites*. Position is the “environment- superselected preferred observable”. †
- It is difficult to predict effective damping on vibronic energy eigenstates.

The Reduced Hierarchy Equation of Motion approach requires no diagonalization: $\mathrm{Tr}_{Env}[\rho(t)]$ is propagated in the site basis.

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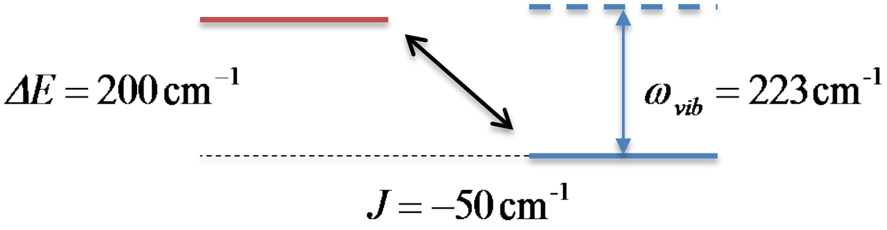
†M. Schlosshauer. “*Decoherence and the Quantum-to-Classical Transition.*” Springer, 2008. p74

POPULATION DYNAMICS

Akihito Ishizaki

$S = 0.025 \quad T = 300\,\mathrm{K}$

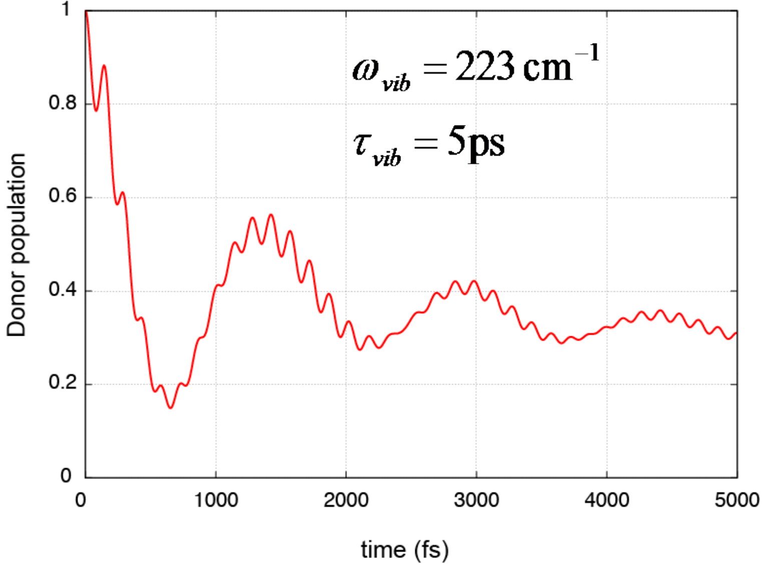


$\Delta E = 200\,\mathrm{cm}^{-1}$

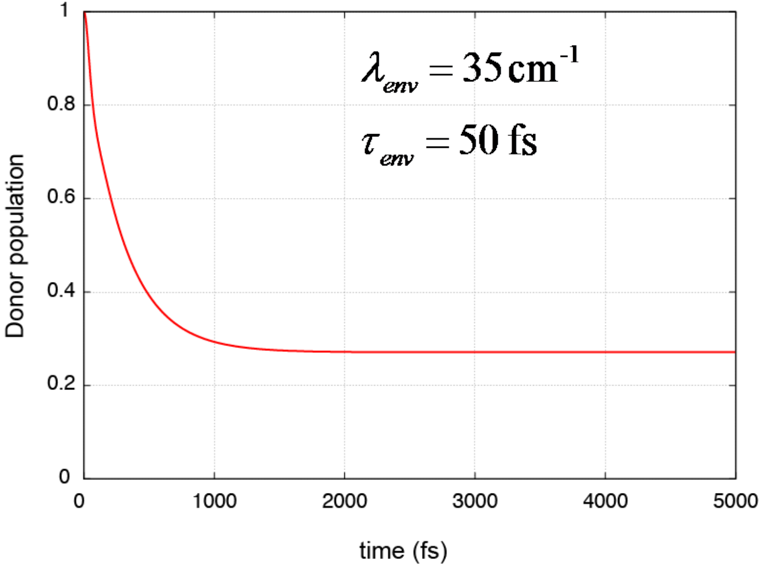
$\omega_{vib} = 223\,\mathrm{cm}^{-1}$

$J = -50\,\mathrm{cm}^{-1}$

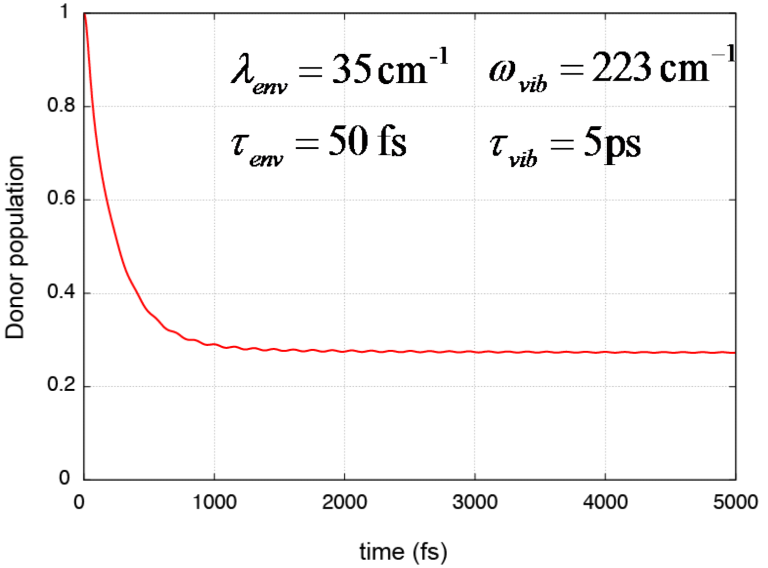
Only vibrational contribution



Only environmental contribution



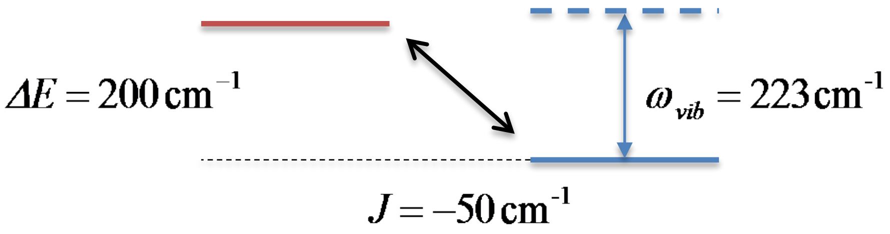
Environmental + vibrational contributions



POPULATION DYNAMICS

Akihito Ishizaki

$S = 0.1 \quad T = 300\,\mathrm{K}$



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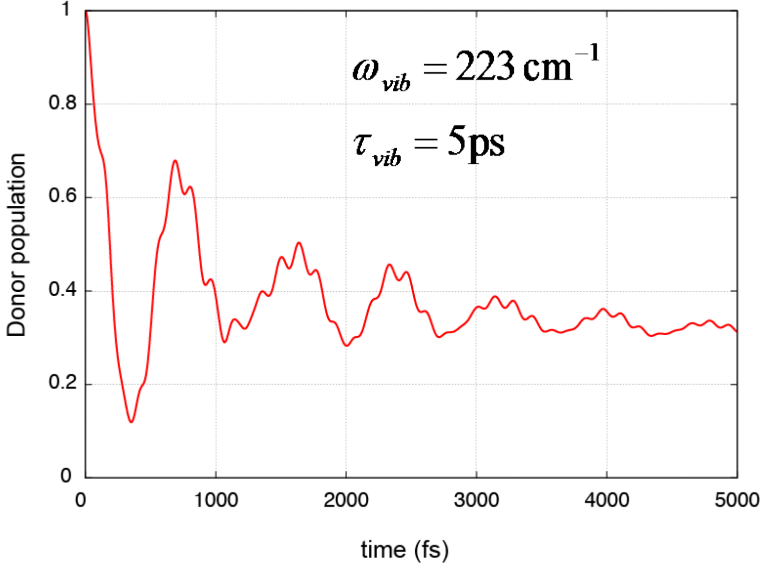
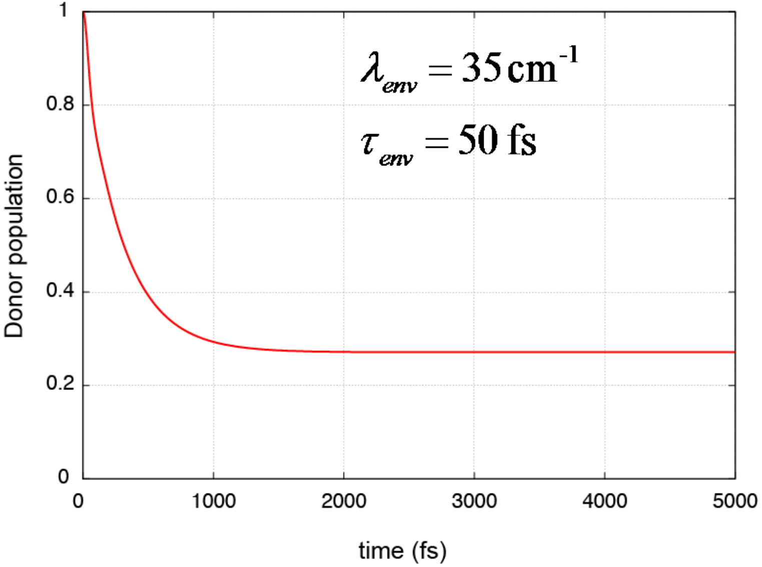
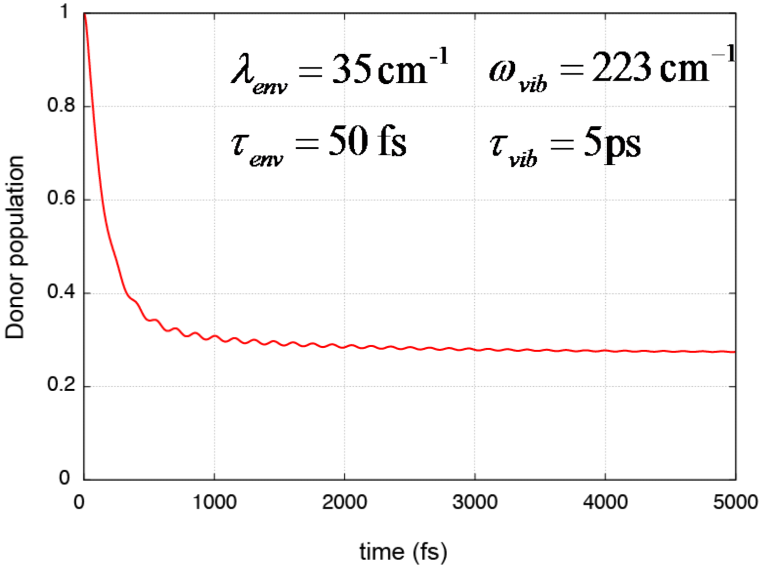


Only environmental contribution



Environmental + vibrational contributions



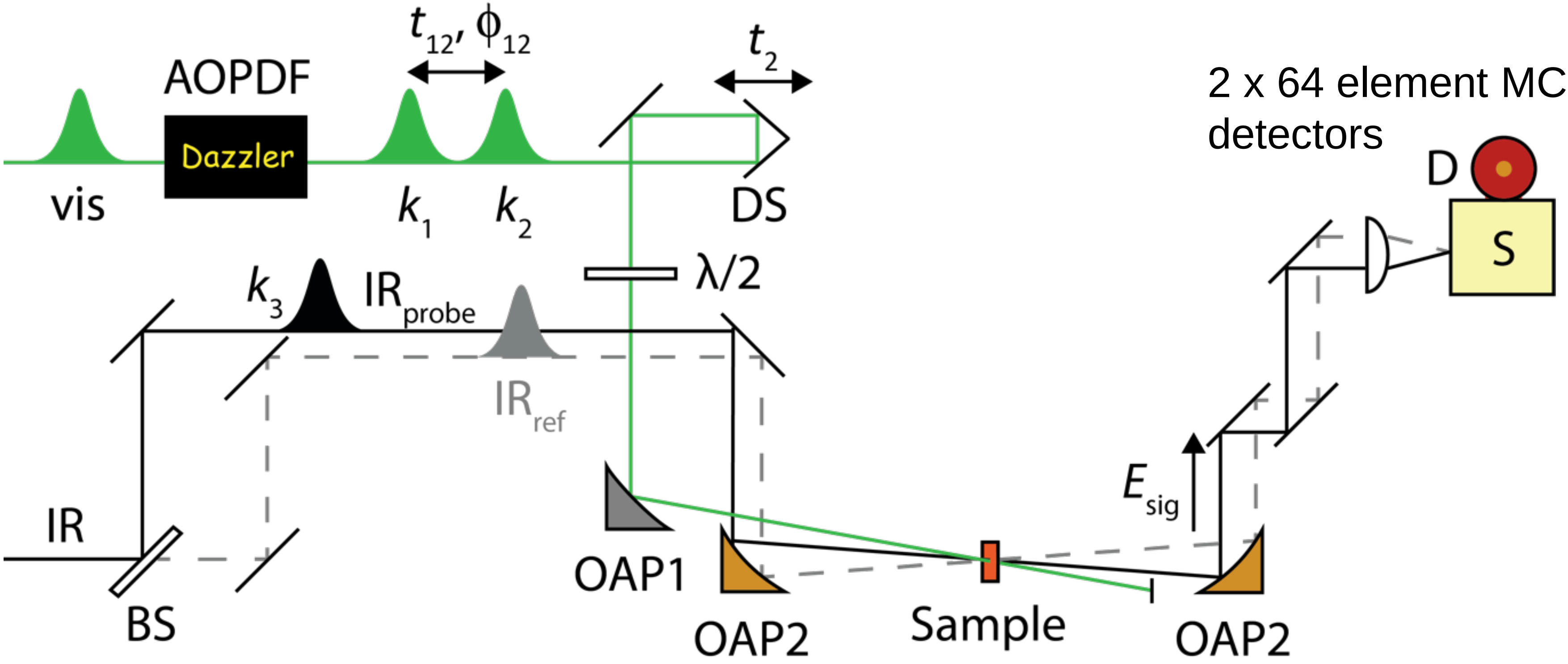
What do we mean by energy transfer ?

Are there new experiments that would help ?

Experimental setup

k_1 and k_2: 25 fs, 1300 cm^{-1}, 200 nJ

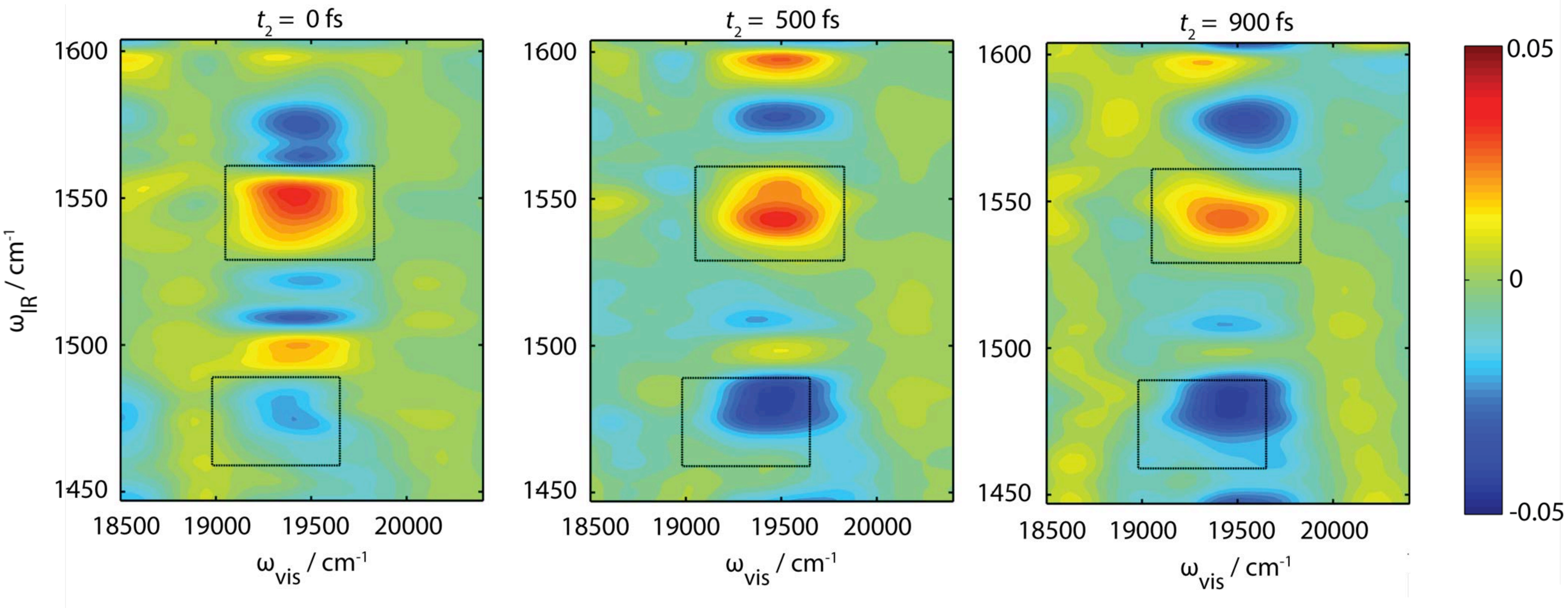
2 x 64 element MCT detectors



k_3: ~90 fs, ~200 cm^{-1}, 100 nJ

250 ⌠m pathlength, OD ~ 0.25

2D-EV of DCM/DMSO spectra as a function of t_2



- Ground state vibrations (positive) show little evolution as a function of t_2
- Excited state vibrations (negative) blue shift in both electronic and vibrational axes

But isn’t the sun an incoherent light source ?

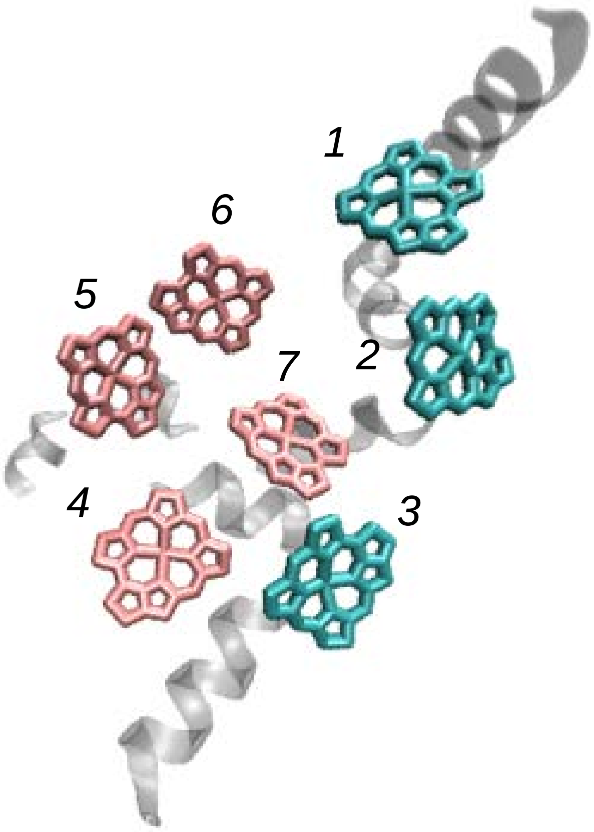
Akihito Ishizaki
Gabriela Schlau-Cohen
Emily Jane Sylak-Glassman
Eleonora De Re
Hui Dong
Kapil Amarnath
Doran Bennett
Arijit De
Daniele Monahan
Tom Oliver
Nick Lewis

Kris Niyogi

DOE, BES Chemical Sciences Geosciences and Biosciences

Greg Scholes
Rienk van Grondelle
Alexandra Olaya-Castro

A Mixed Quantum/Classical Equations of Motion Approach



$$|\psi(t)\rangle = \sum_m c_m(t)|m\rangle$$

Excitation transfer is described with the Schrödinger equation,

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \big[H_{\rm ex} + H_{\rm ex-env}(t)\big]|\psi(t)\rangle$$

The environment follows the classical Hamilton equations,

$$\frac{\mathrm{d}}{\mathrm{d}t}q_{m\xi}(t) = \frac{\partial}{\partial\hbar p_{m\xi}}\big[H_{\rm env} + \underline{\langle\psi(t)|H_{\rm ex-env}|\psi(t)\rangle}\big]$$

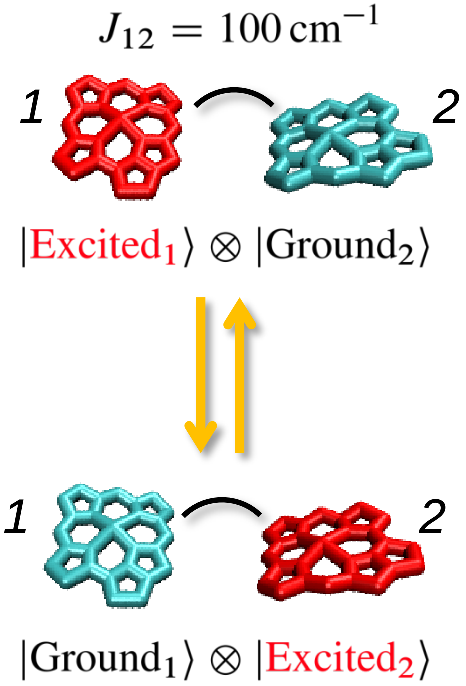
$$\frac{\mathrm{d}}{\mathrm{d}t}\hbar p_{m\xi}(t) = -\frac{\partial}{\partial q_{m\xi}}\big[H_{\rm env} + \underline{\langle\psi(t)|H_{\rm ex-env}|\psi(t)\rangle}\big]$$

Generally, it is difficult to combine the fundamentally different descriptions of nature provided by quantum and classical mechanics. In order for such contradictions to be minimized enough, we assume

$$\langle\psi(t)|H_{\rm ex-env}|\psi(t)\rangle = 0$$

This corresponds to the assumptions of the temperature-independent Lindblad equation or the Haken-Strobl model (infinite-temperature limit), which are extensively employed for examining quantum effects in photosynthesis.

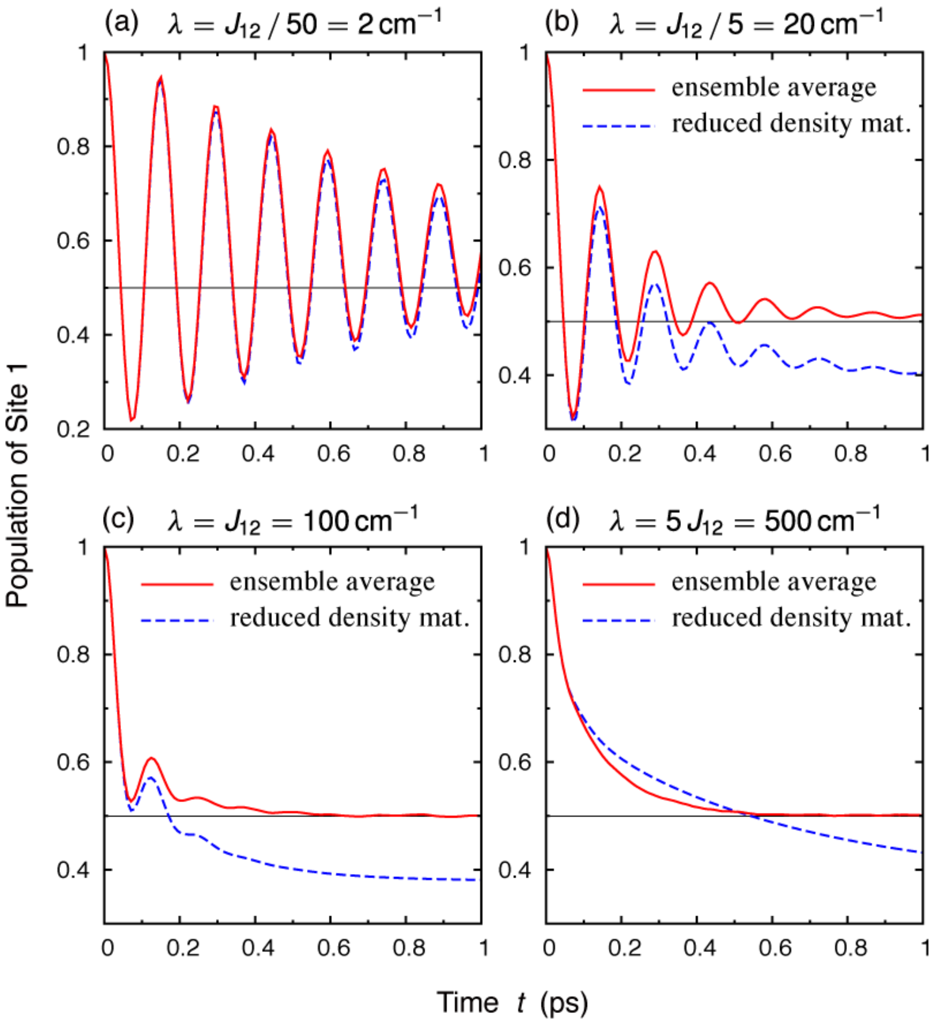
Reduced Density Matrix and Ensemble Average



$J_{12} = 100\,\mathrm{cm}^{-1}$

$|\mathrm{Excited}_1\rangle \otimes |\mathrm{Ground}_2\rangle$

$|\mathrm{Ground}_1\rangle \otimes |\mathrm{Excited}_2\rangle$



Ishizaki & Fleming,
J. Chem Phys. **130**, 234111 (2009).

50,000 trajectories

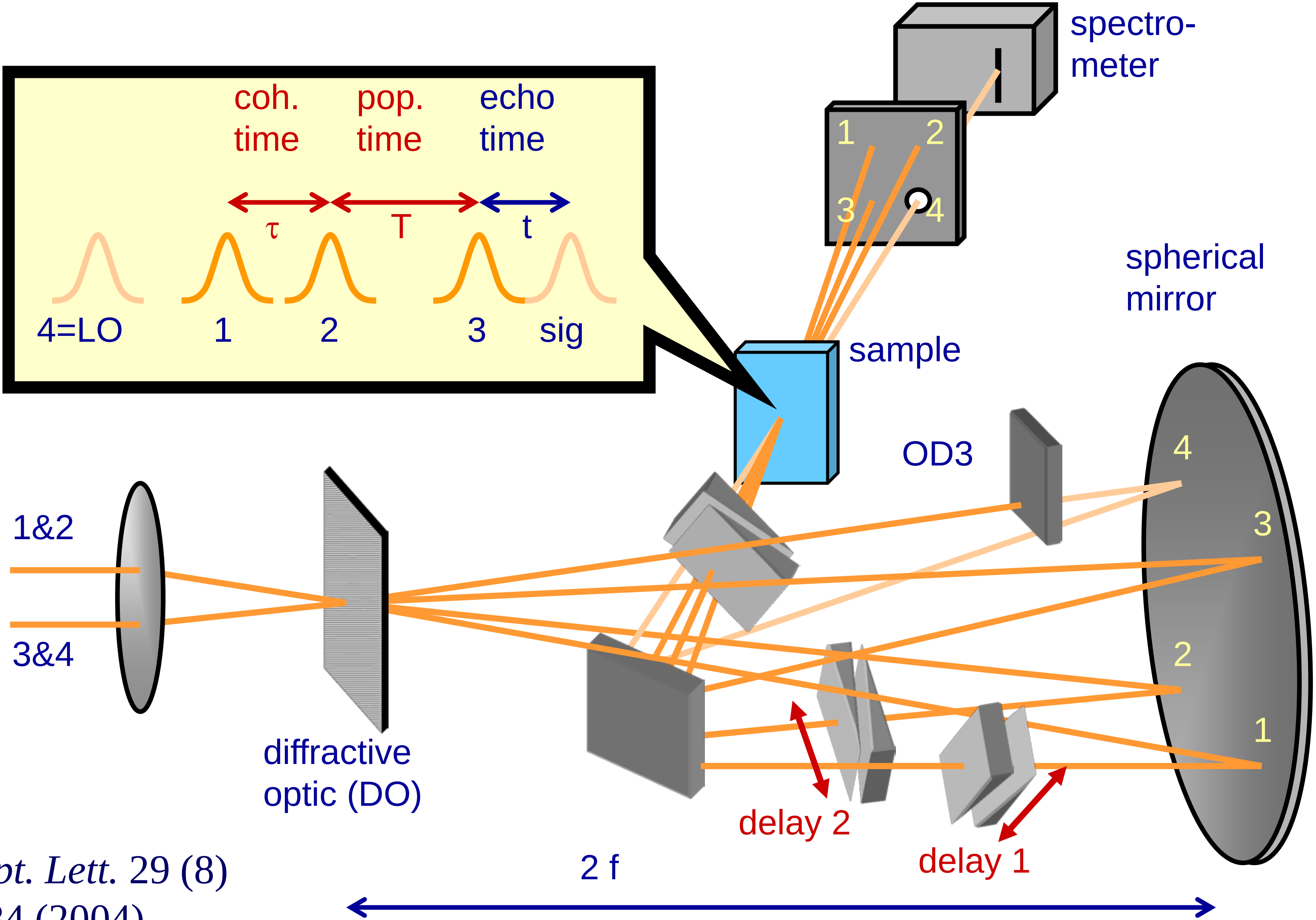
$\Omega_1 - \Omega_2 = 100\,\mathrm{cm}^{-1}$

$\tau_1^{\mathrm{rxn}} = \tau_2^{\mathrm{rxn}} = 100\,\mathrm{fs},\ \ T = 300\,\mathrm{K}$

1,000 phonon modes per pigment

The behavior of the reduced density matrix can be interpreted as the ensemble average of the energy transfer dynamics in individual proteins.

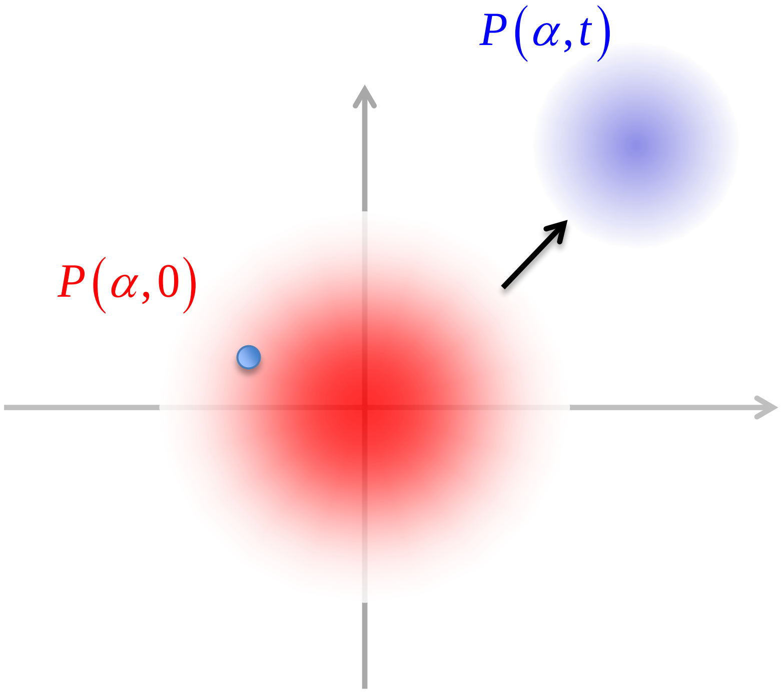
Two-Dimensional Heterodyne Spectroscopy



Opt. Lett. 29 (8)
884 (2004)

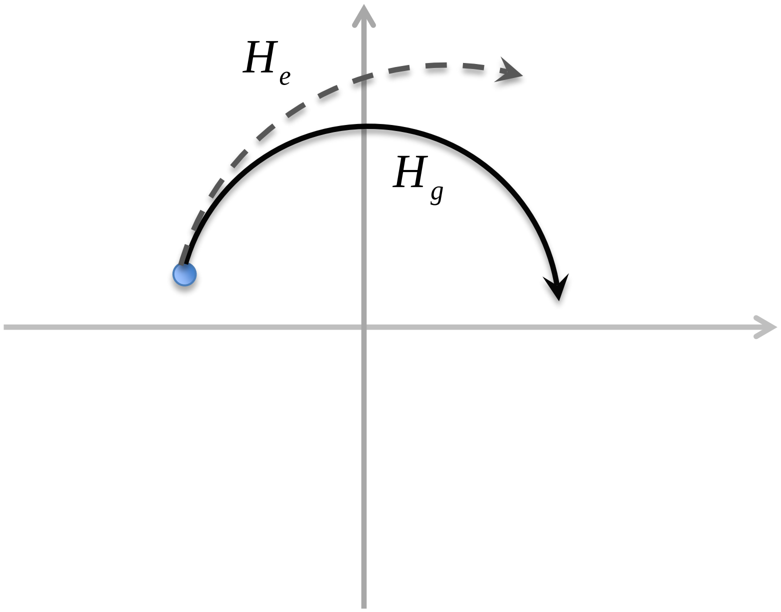
Density Matrix vs Wave-function

Ensemble
Time evolution of the thermal state in coherent state space



$$P(\alpha,0)\propto \exp[-|\alpha|^2/\langle n\rangle]$$

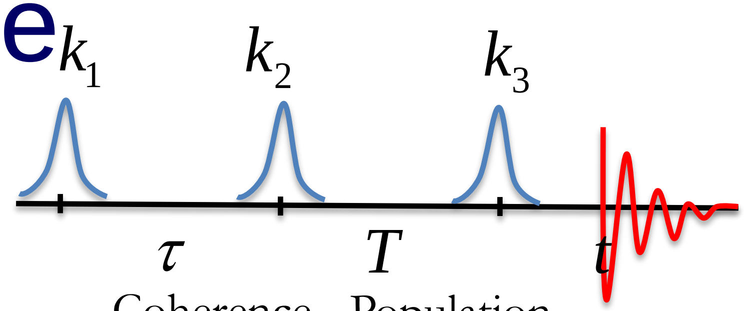
Single molecule
Time evolution of a coherent state



$|\alpha\rangle$ Chosen from the distribution $P(\alpha,0)$

Third-order Response Function for Photon Echo of a Single Molecule

System + Environment



Coherence time

Population time

$$\left|\psi(t)\right\rangle = \sum_n c_n(t)\left|\varphi_n\right\rangle_{\text{sys}} \otimes \left|\vartheta_n\right\rangle_{\text{env}}$$

Perturbation according to interaction with pulse

$$\left|\psi(\tau,T,t)\right\rangle = \sum_{z=0}^{\infty}\left|\psi^{(z)}(\tau,T,t)\right\rangle$$

Single molecule signal

$$\begin{aligned} I(\tau,T,t) &\propto \left|\left\langle\psi^{(1)}\right|\mu\left|\psi^{(2)}\right\rangle + \left\langle\psi^{(2)}\right|\mu\left|\psi^{(1)}\right\rangle\right| \\ &= R_1\left(\tau,T,t;\left\{\alpha_\xi\right\}\right) \\ &+ R_2\left(\tau,T,t;\left\{\alpha_\xi\right\}\right) + h.c. \end{aligned}$$

New term arising from initial state of environment

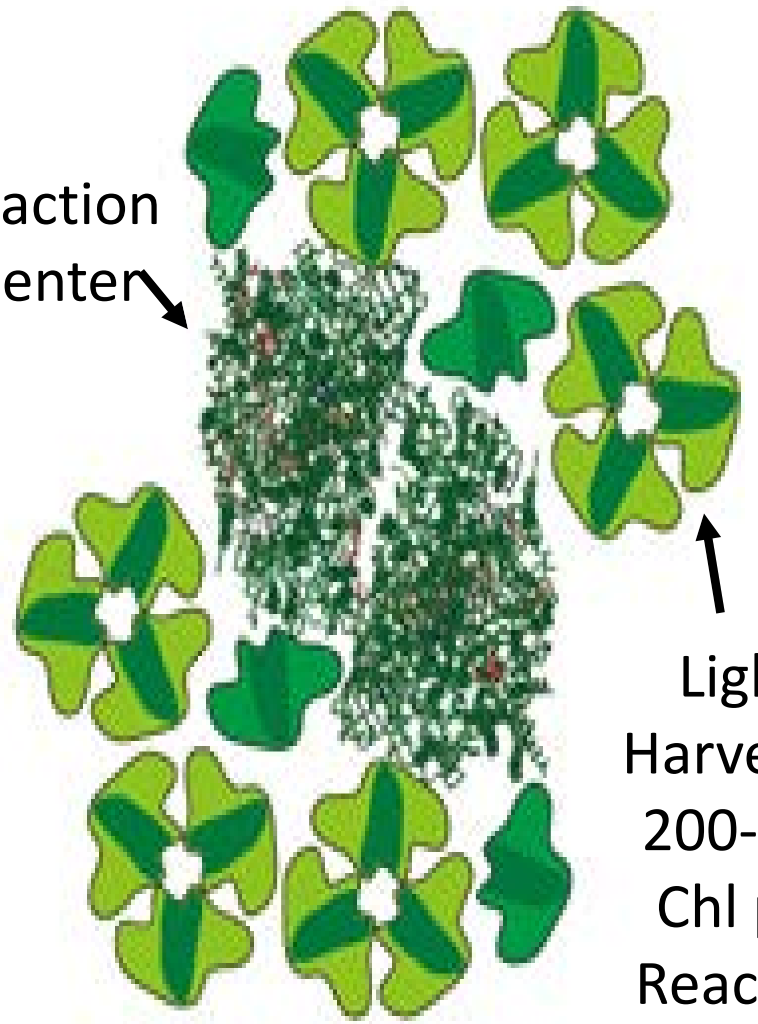
Ensemble signal

$$I(\tau,T,t) \propto \left|\text{Tr}_{\text{sys+env}}\left[\mu\rho^{(3)}(\tau,T,t)\right]\right|$$

Average over initial state

H.Dong and GRF, (2013) JPC B in press

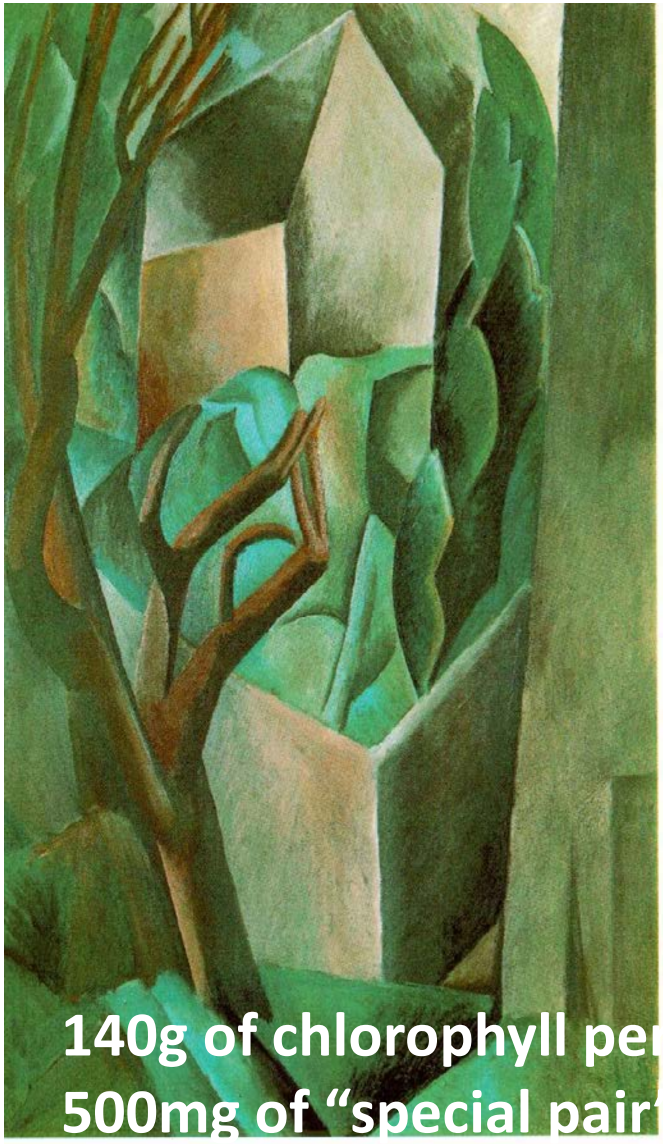
Photosystem II is the most sophisticated nano machine on earth



Reaction Center

Light Harvester 200-300 Chl per Reaction Center

Pablo Picasso – House and Trees
Paris, Winter 1908



140g of chlorophyll pe
500mg of “special pair

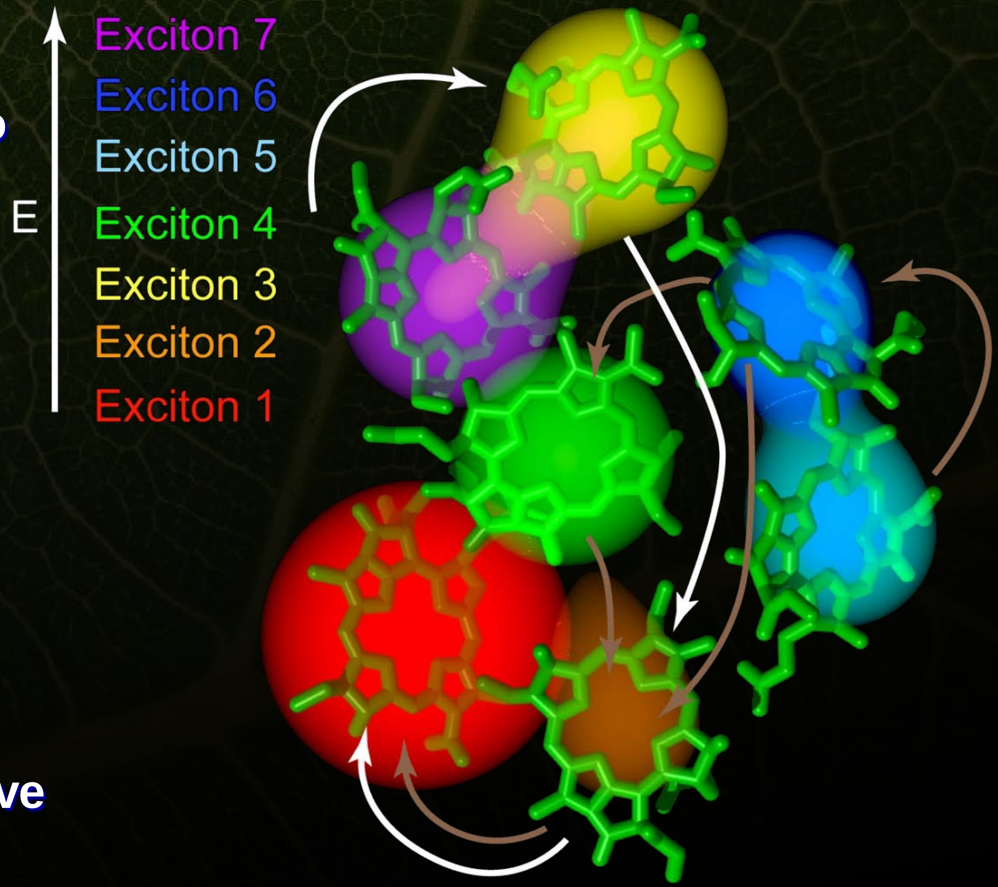
Image modified from: J Minagawa (2013). Front. Plant Sci.

Quantum Computing?

- Can FMO act as a dedicated quantum computational device?
- No strict one-to-one mapping onto quantum search algorithms such as Grover's algorithm

But

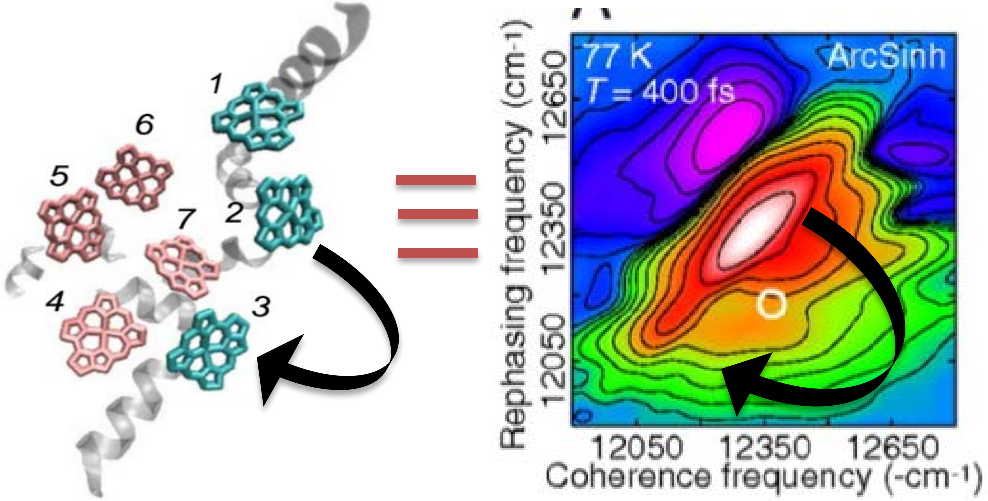
  - Coherent superposition states allow the complex to sample many states very rapidly.
  - A trap ' decoheres' the system
- Is the system 'designed' to preserve coherence?

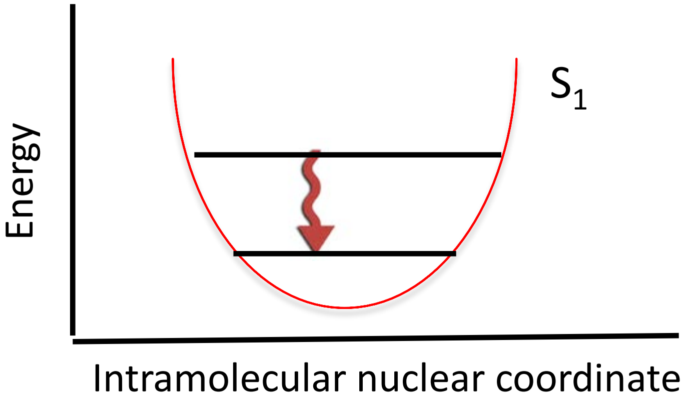


"Quantum Mechanics Helps in Searching for a Needle in a Haystack."
Grover, *PRL*, **79**:325 1997

How do we measure energy transfer?

Spectroscopically measured exciton relaxations show energy transfer among pigments only if the location of excitons is known.



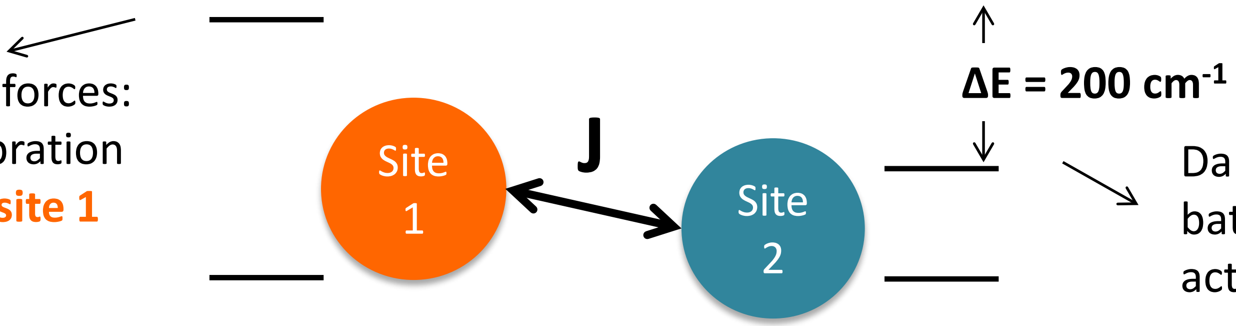


In some systems, localized vibronic states relax while energy remains on the same pigments.

(Similarly: decoherence only describes relocalization if the coherence was prepared between states that are separated in space.)

Simulating vibronic 2D-ES spectra with a bath – Hierarchy Equations Approach

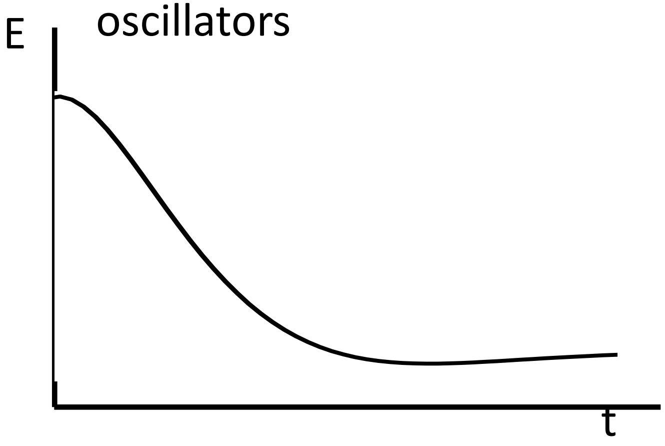
Damping forces:
bath + vibration
acting at **site 1**



Damping forces:
bath + vibration
acting at **site 2**

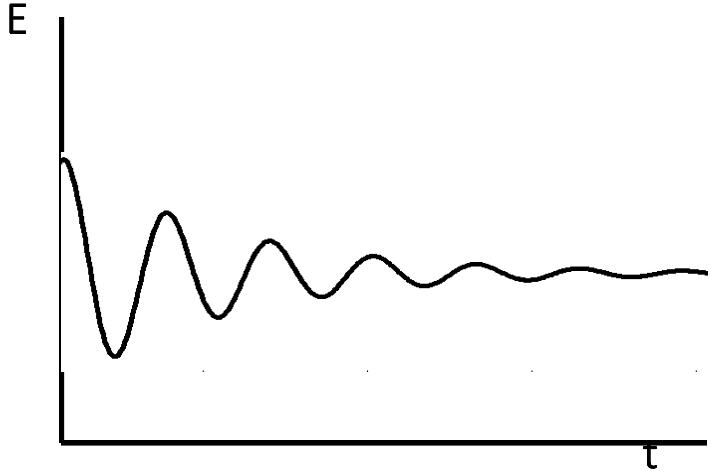
Uncorrelated damping forces acting at each pigment site:

Bath of <u>overdamped</u> brownian oscillators



+

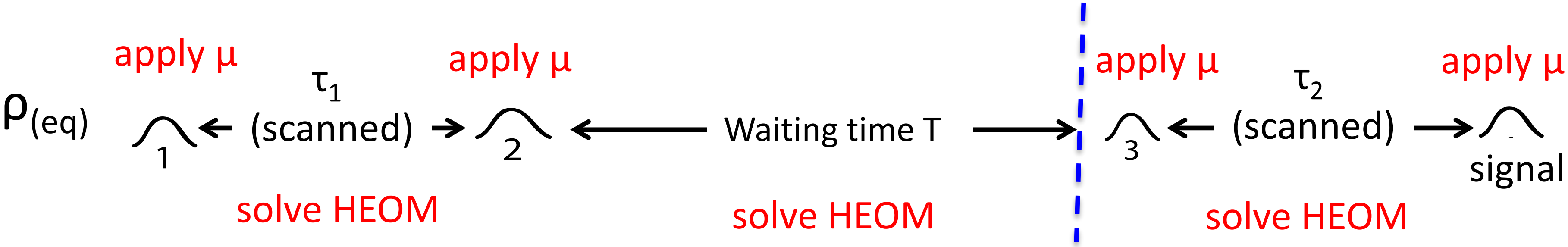
<u>One underdamped</u> vibrational mode



Concerted study in site and exciton bases:

Dipole operator μ gives spectroscopic response – the experimental observable.
Site population operator P_{acc} gives the amount of excitation at the destination site.

PREPARATION | ENERGY TRANSFER/RELAXATION | MEASUREMENT



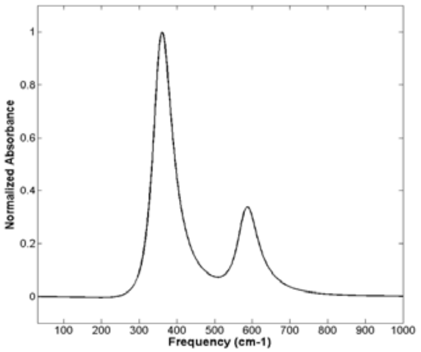
$\rho_{(eq)}$

apply μ → 1 ← τ_1 (scanned) → apply μ → 2 ← Waiting time T → apply μ → 3 ← τ_2 (scanned) → apply μ → signal

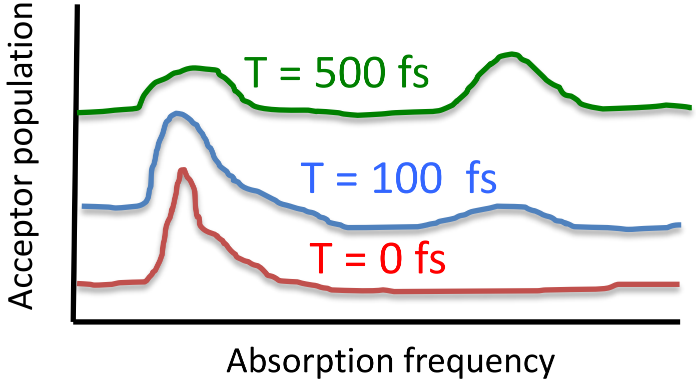
solve HEOM | solve HEOM | solve HEOM

apply P_{acc}

2-point correlation gives linear absorption spectrum:



Simulated “site population spectrum” shows energy transfer over T



4-point correlation gives 2D-ES spectrum:

Nonrephasing Spectrum at T=0