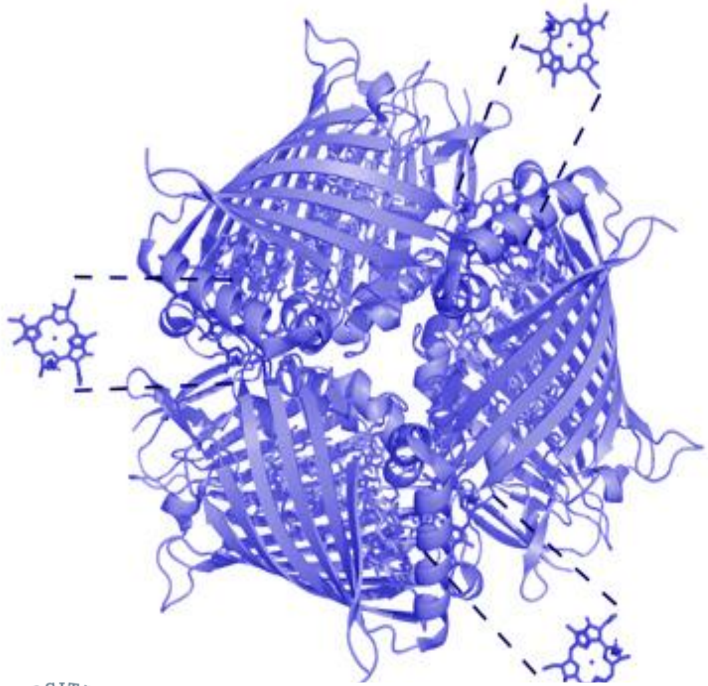
Coherent Effects in Photosynthetic Complexes

Principles of noise assisted transport and the origin of long-lived coherences

Susana Huelga (Universität Ulm, Germany)



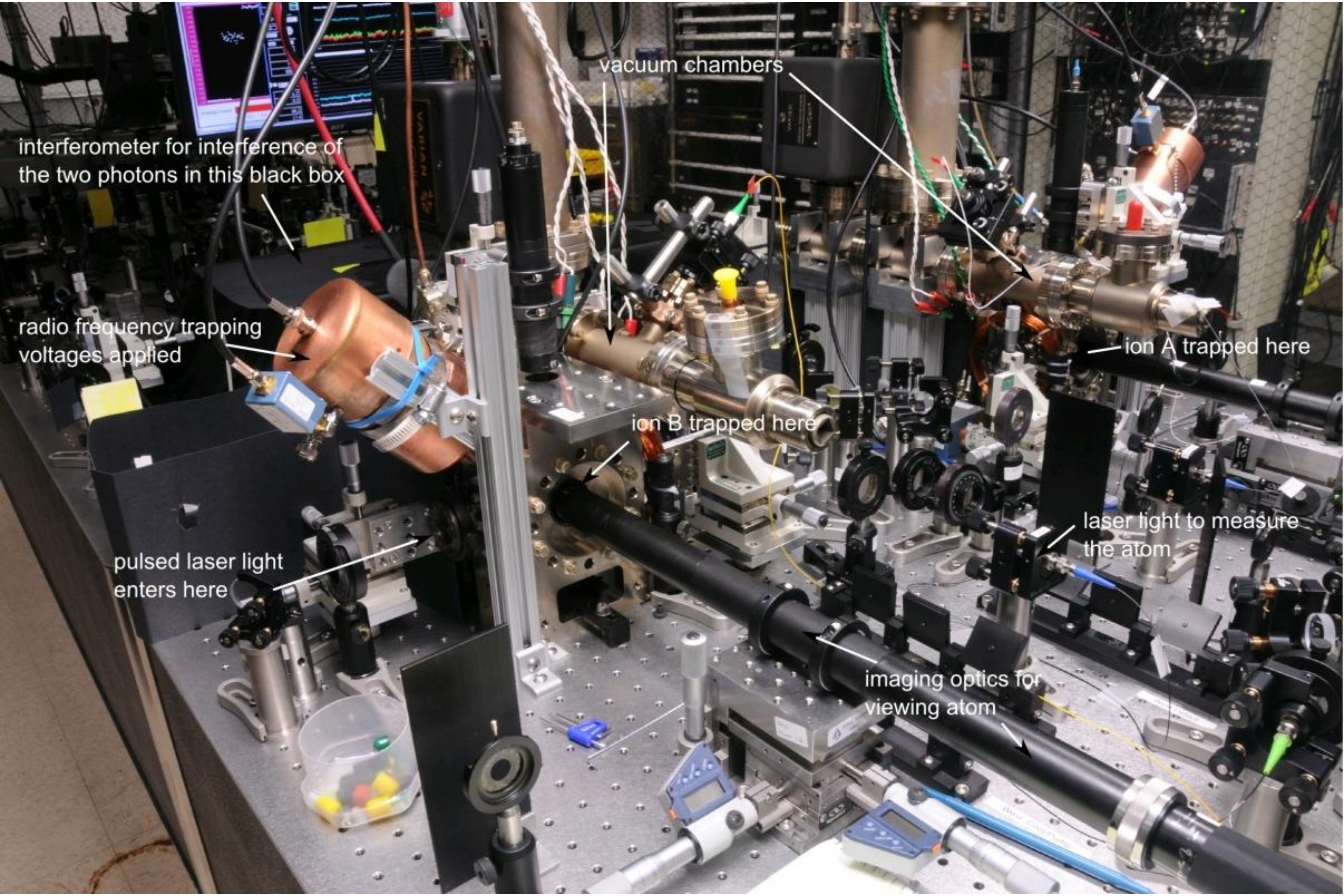
UNIVERSITÄT ULM · SCIENDO · DOCENDO · CURANDO ·

ulm university universität uulm

44th Symposium on Mathematical Physics, Torun, June 20-24 (2012)

(Non-trivial) Quantum Effects in Biology??

NJP **13** 115002 (2011)
Focus on quantum effects and noise in biomolecules
GR Fleming, SF Huelga and MB Plenio Eds



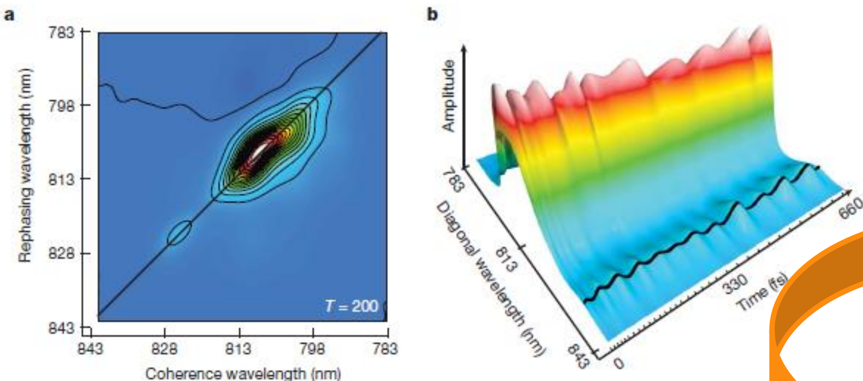
vacuum chambers
interferometer for interference of
the two photons in this black box
radio frequency trapping
voltages applied
ion A trapped here
ion B trapped here
laser light to measure
the atom
pulsed laser light
enters here
imaging optics for
viewing atom

nature
Vol 446|12 April 2007|doi:10.1038/nature05678

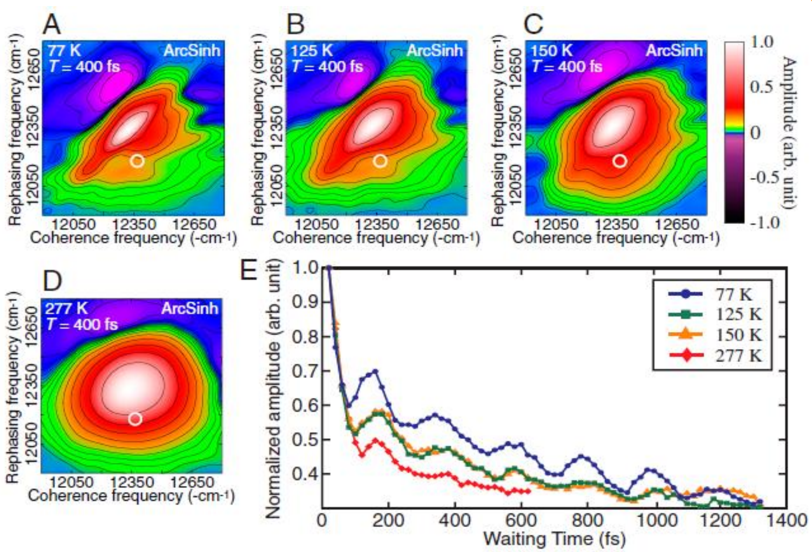
LETTERS

Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems

Gregory S. Engel[1,2], Tessa R. Calhoun[1,2], Elizabeth L. Read[1,2], Tae-Kyu Ahn[1,2], Tomáš Mančal[1,2]†, Yuan-Chung Cheng[1,2], Robert E. Blankenship[3,4] & Graham R. Fleming[1,2]



Experimental evidence at cryogenic and physiological temperatures indicates the presence of quantum coherence



PNAS

www.pnas.org/cgi/doi/10.1073/pnas.1005484107

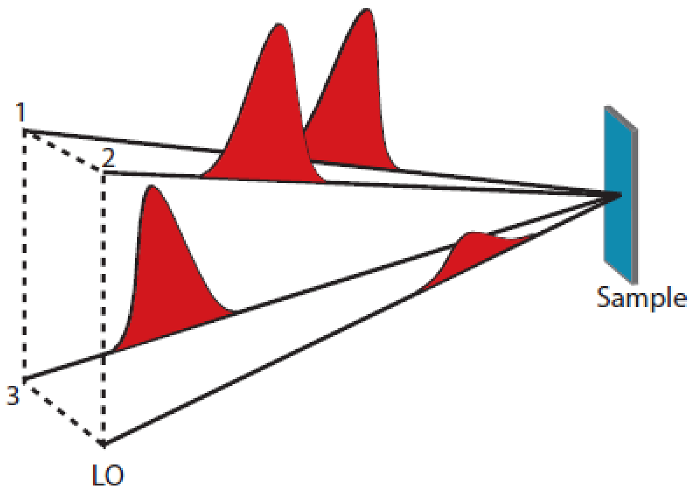
Long-lived quantum coherence in photosynthetic complexes at physiological temperature

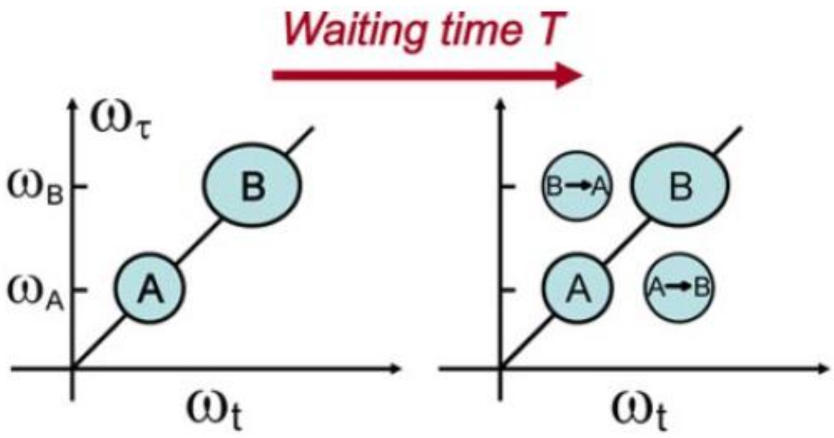
Gitt Panitchayangkoon[a], Dugan Hayes[a], Kelly A. Fransted[a], Justin R. Caram[a], Elad Harel[a], Jianzhong Wen[b], Robert E. Blankenship[b], and Gregory S. Engel[a,1]

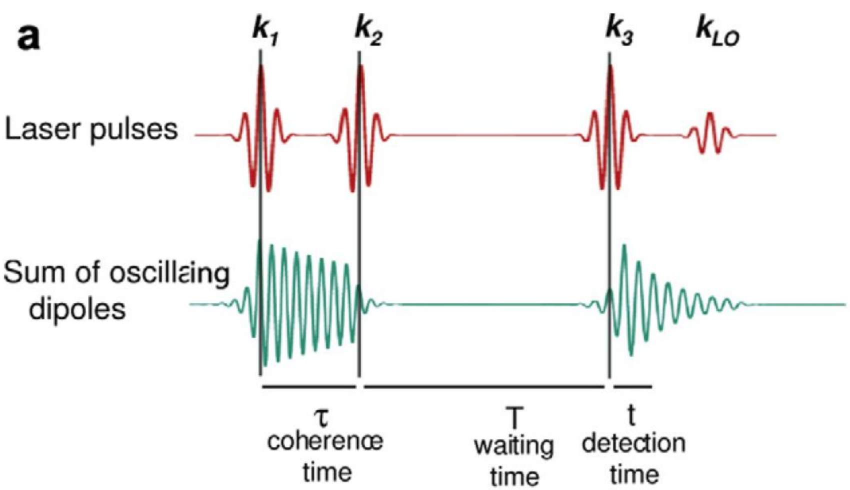
[a]Department of Chemistry and The James Franck Institute, University of Chicago, Chicago, IL 60637; and [b]Departments of Biology and Chemistry, Washington University, St. Louis, MO 63130

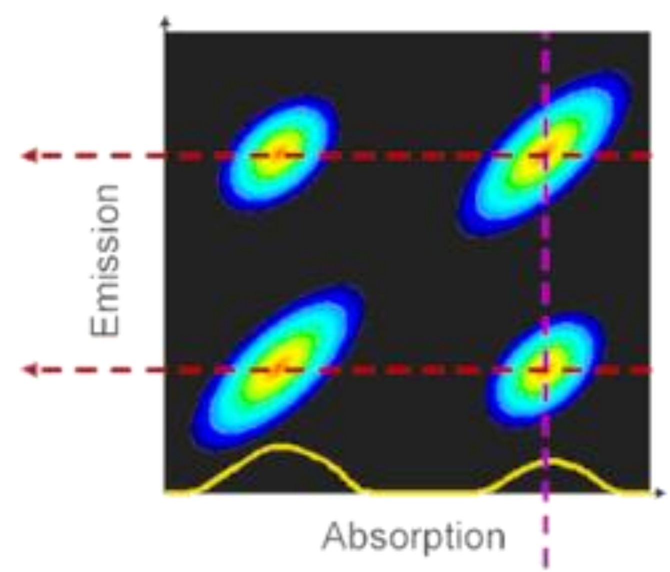
Other results: Scholes (Toronto), van Hulst (ICFO)...

2D Spectroscopy

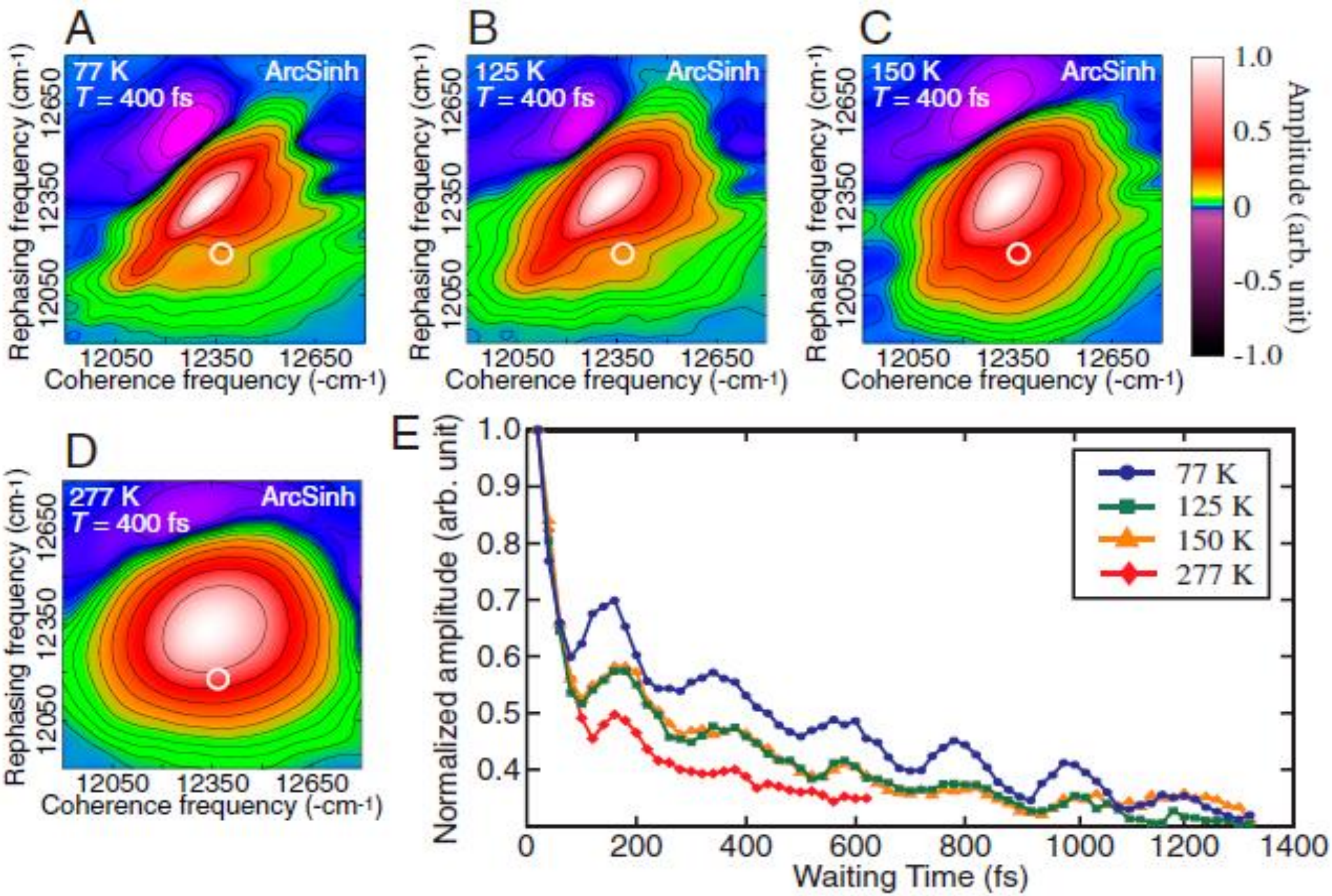




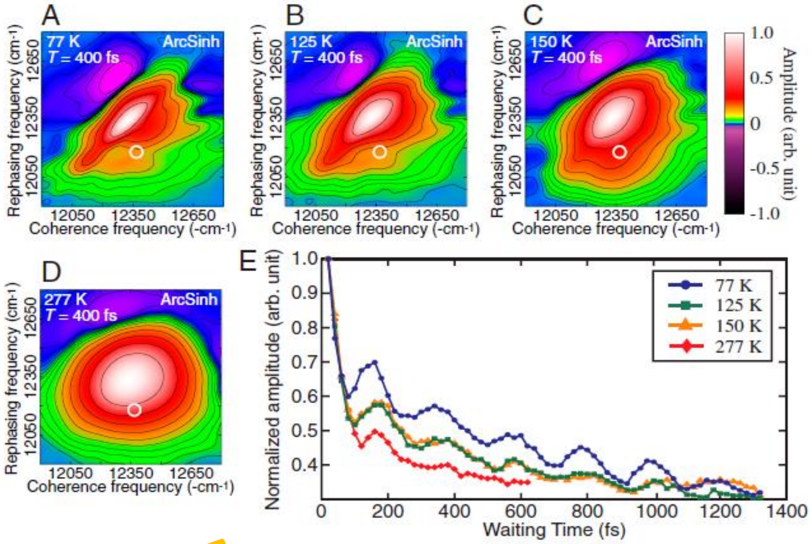




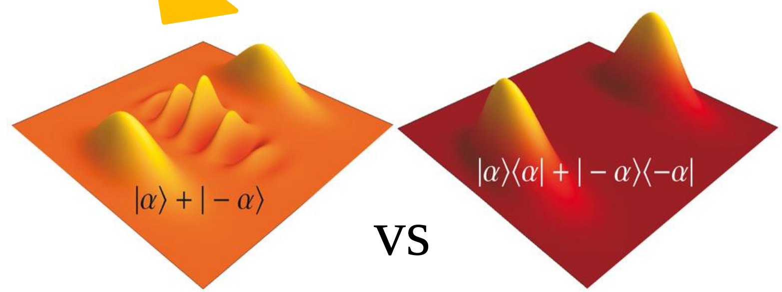
G.S. Schlau-Cohen, T.R. Calhoun, N.S. Ginsberg, E.L. Read, M. Ballottari, R. Bassi, R. van Grondelle, G.R. Fleming, J. Phys. Chem. B 113 (2009) 15352.



GS Engel group, PNAS 2011



Mesoscopic quantum coherence in a (very) noisy environment

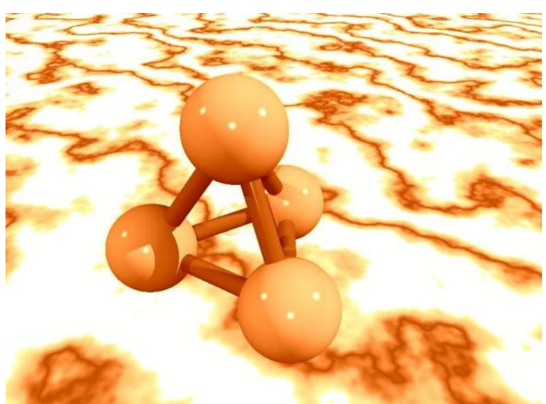


vs

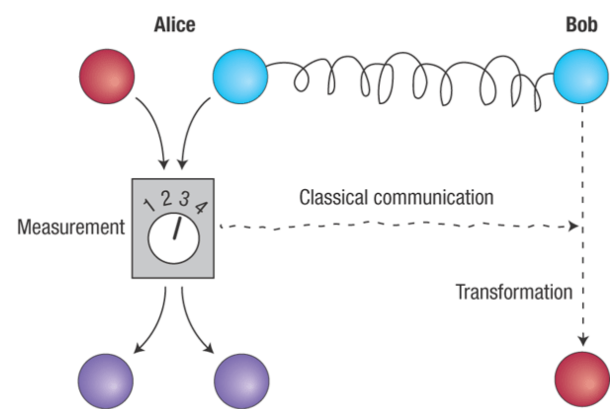
And beyond

A fundamental question arises: Is there any link between coherence and biological function?

Do/could quantum features **facilitate** processes of biological relevance?

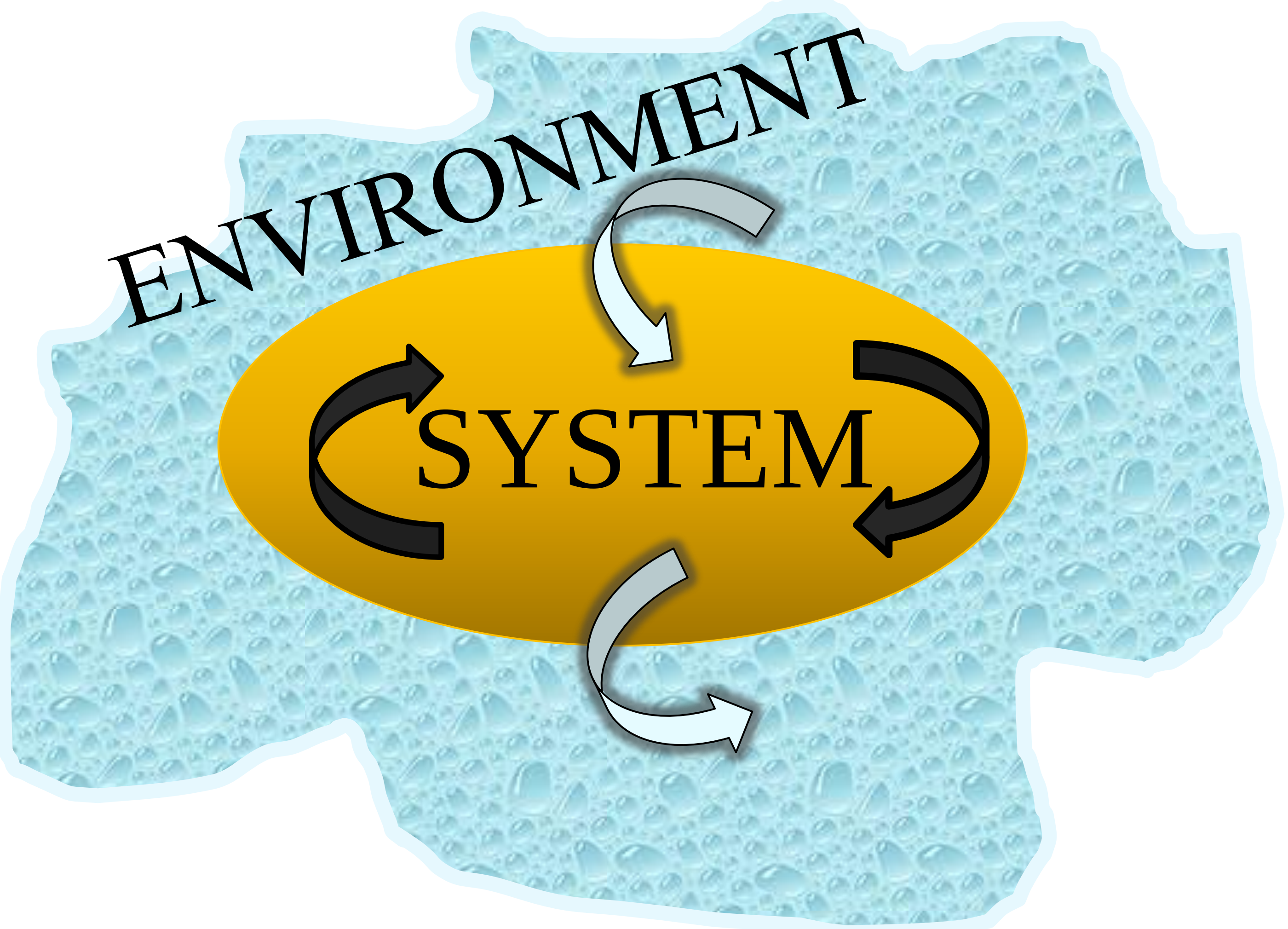


vs



More prosaic:

New perspectives for non-equilibrium open quantum systems

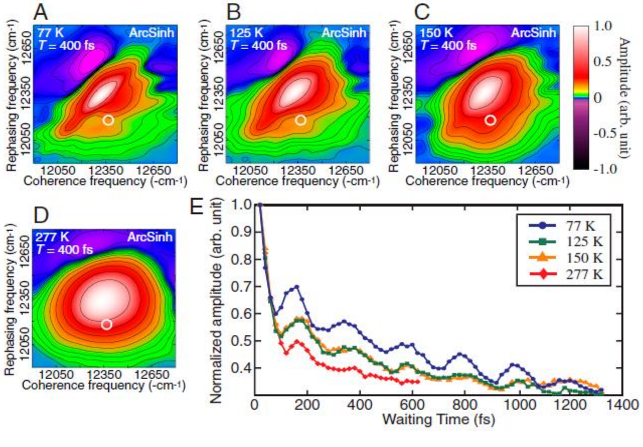


Careful **interplay between coherent and *noisy* interactions** is key for keeping quantum traits and for them to survive (even) in the steady state

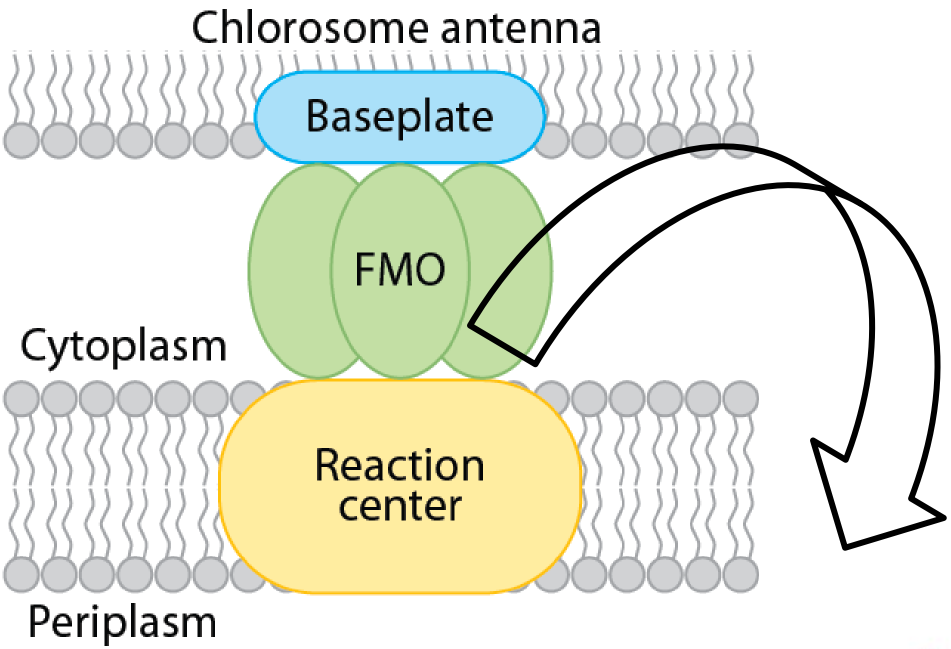
Outline

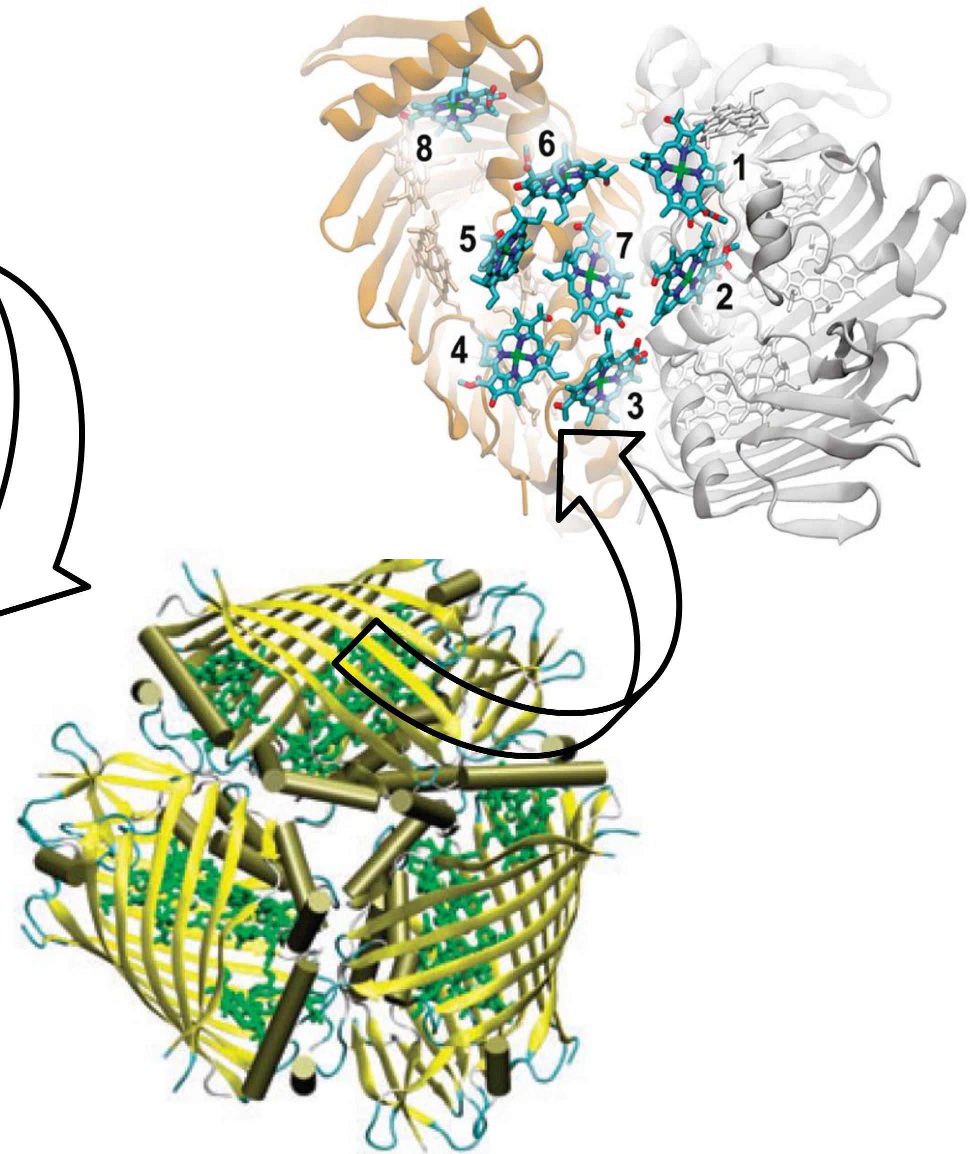
Noise assisted transport: Fundamental mechanisms
The concept of *phonon antenna*

Long lived coherence
How can quantum coherence persist in a *wet* and *hot* environment?



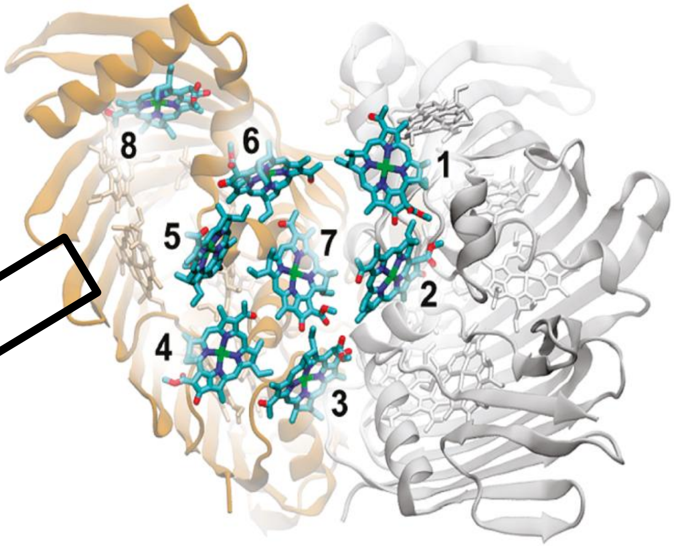
Fenna-Matthew-Olson (FMO) complex

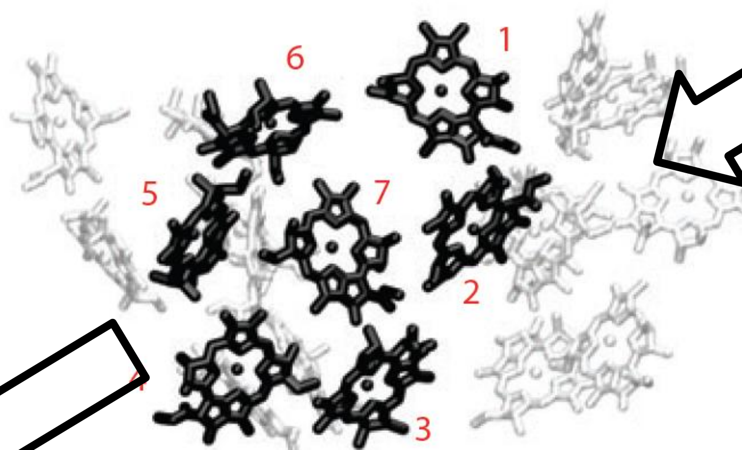


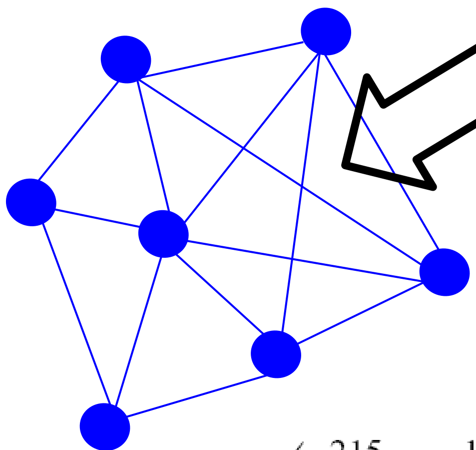


- R.E. Fenna and B.W. Matthews, *Nature* **258** 573 (1975)
- Y.-C. Cheng & G.R. Fleming, Annual Reviews of Phys. Chem. 2009
- Schmidt am Busch et al, *The Eighth Bacteriochlorophyll Completes the Excitation Energy Funnel in the FMO Protein.* J. Phys. Chem. Lett. **2,** 93 (2011)

Deconstructing the transport dynamics





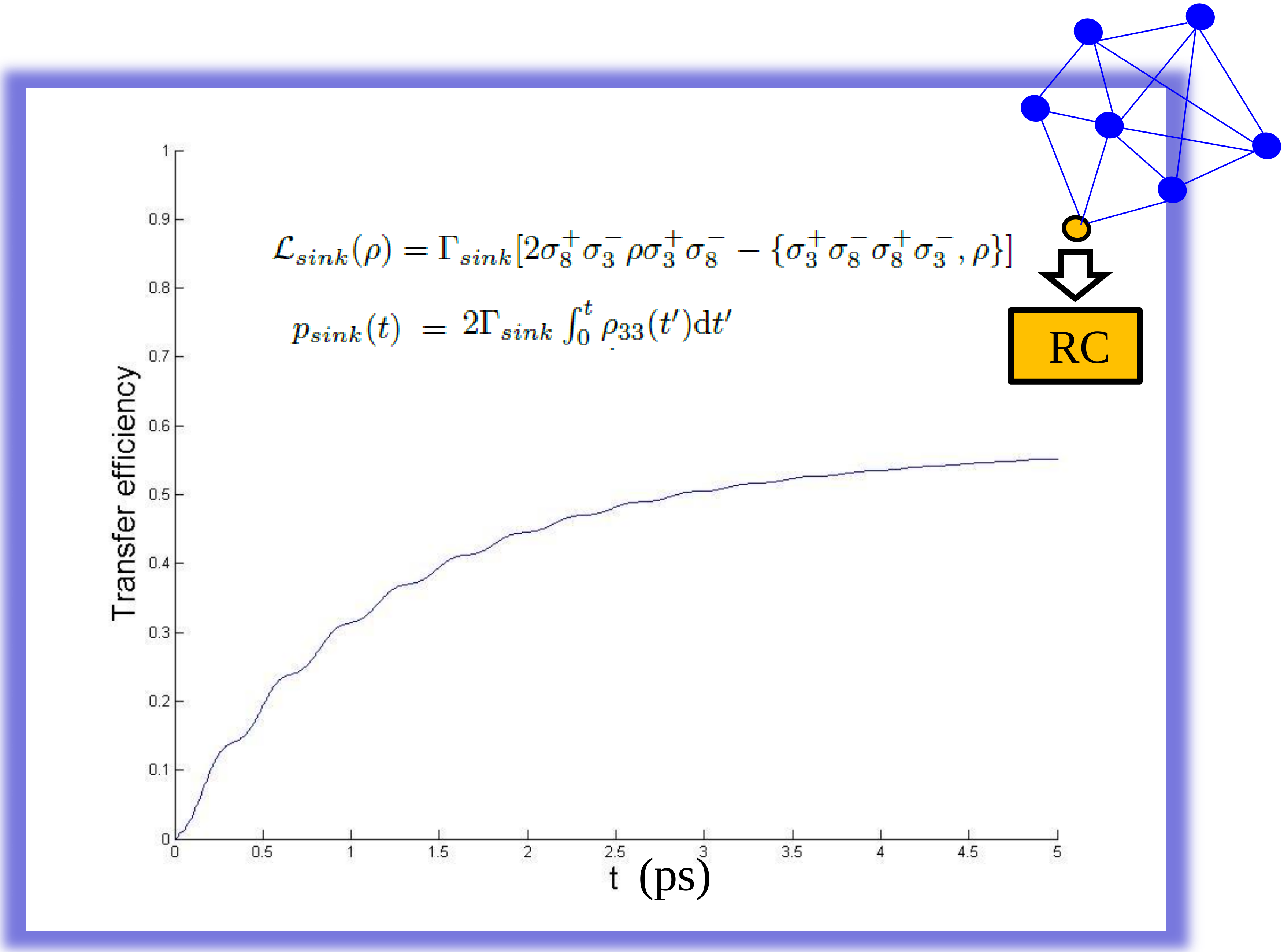


$$H = \sum_{j=1}^{N} \hbar\omega_j \sigma_j^+ \sigma_j^- + \sum_{j \neq l} \hbar v_{j,l} (\sigma_j^- \sigma_l^+ + \sigma_j^+ \sigma_l^-)$$

$$H = \begin{pmatrix} 215 & -104.1 & 5.1 & -4.3 & 4.7 & -15.1 & -7.8 \\ -104.1 & 220.0 & 32.6 & 7.1 & 5.4 & 8.3 & 0.8 \\ 5.1 & 32.6 & 0.0 & -46.8 & 1.0 & -8.1 & 5.1 \\ -4.3 & 7.1 & -46.8 & 125.0 & -70.7 & -14.7 & -61.5 \\ 4.7 & 5.4 & 1.0 & -70.7 & 450.0 & 89.7 & -2.5 \\ -15.1 & 8.3 & -8.1 & -14.7 & 89.7 & 330.0 & 32.7 \\ -7.8 & 0.8 & 5.1 & -61.5 & -2.5 & 32.7 & 280.0 \end{pmatrix}$$

Adapted from Adolphs&Renger 2006
Plenio&Huelga, New J. Phys. **10**, 113019 (2008)

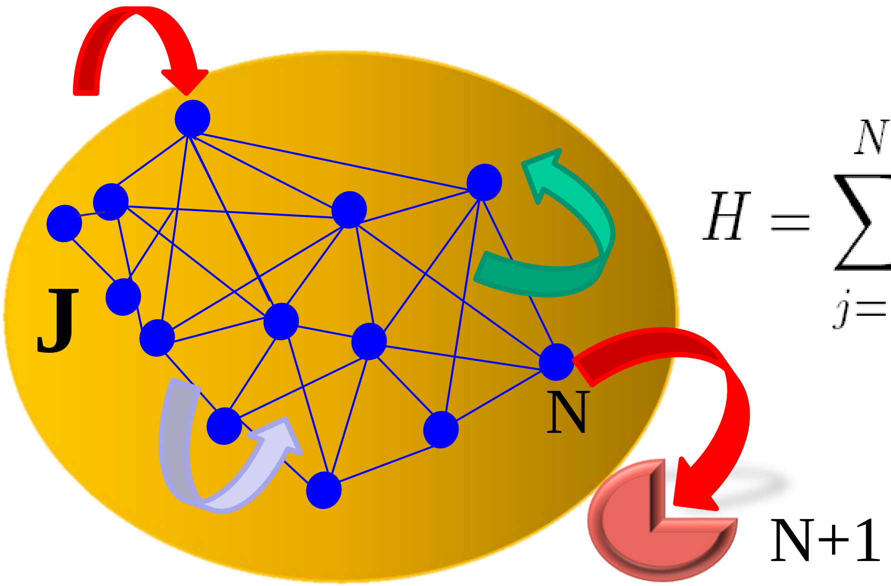
(Units 1.2414 10^{-4} eV)



$$\mathcal{L}_{sink}(\rho) = \Gamma_{sink}[2\sigma_8^+ \sigma_3^- \rho \sigma_3^+ \sigma_8^- - \{\sigma_3^+ \sigma_8^- \sigma_8^+ \sigma_3^-, \rho\}]$$

$$p_{sink}(t) = 2\Gamma_{sink} \int_0^t \rho_{33}(t')\mathrm{d}t'$$

Further simplification: Fully Connected Networks (FCN)



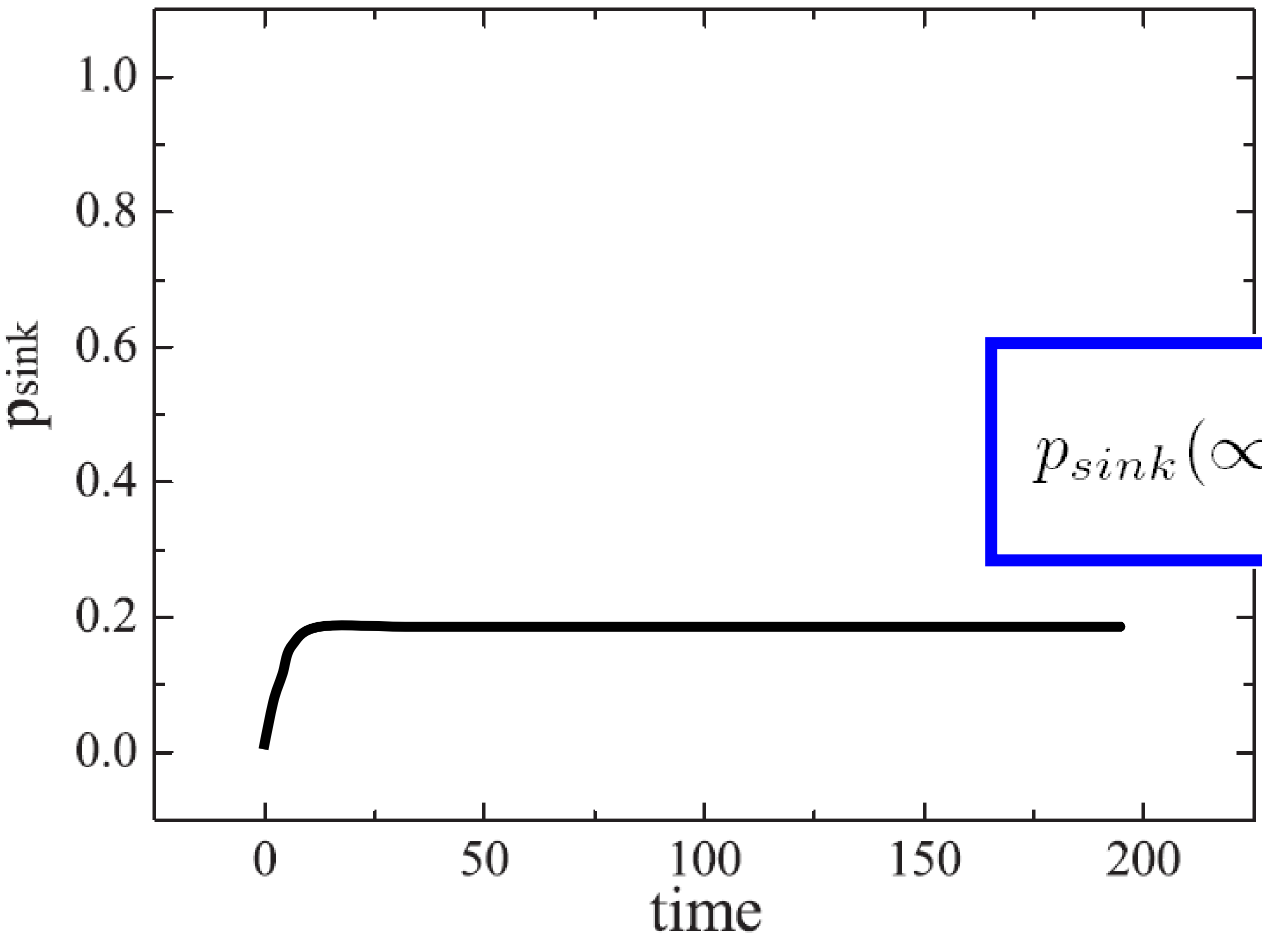
$$H = \sum_{j=1}^{N} \hbar\omega_j \sigma_j^+ \sigma_j^- + \sum_{j \neq l} \hbar \, \mathbf{J} \left(\sigma_j^- \sigma_l^+ + \sigma_j^+ \sigma_l^- \right)$$

Single irreversible process: population transfer from site N to the sink N+1

$$\mathcal{L}_{sink}(\rho) = \Gamma_{N+1}[2\sigma_{N+1}^+ \sigma_k^- \rho \sigma_k^+ \sigma_{N+1}^- - \{\sigma_k^+ \sigma_{N+1}^- \sigma_{N+1}^+ \sigma_k^-, \rho\}]$$

In a given time T, how much of the initial population in site 1 can be transferred to site N+1 **(trapping site)** and how is the transport affected by noise?

$$p_{sink}(t) = 2\Gamma_{N+1} \int_0^t \rho_{kk}(t')\mathrm{d}t'$$



$$p_{sink}(\infty) = \frac{1}{N-1}$$

$$\Gamma = 0, \; J = 1, \Gamma_{N+1} = 1$$

$$\gamma_i = \omega_i = 0$$

N=7 uniform FCN

Deconstructing the transport dynamics

Opinion: Well, this is obvious

$$H=\begin{pmatrix} 215 & -104.1 & 5.1 & -4.3 & 4.7 & -15.1 & -7.8 \\ -104.1 & 220.0 & 32.6 & 7.1 & 5.4 & 8.3 & 0.8 \\ 5.1 & 32.6 & 0.0 & -46.8 & 1.0 & -8.1 & 5.1 \\ -4.3 & 7.1 & -46.8 & 125.0 & -70.7 & -14.7 & -61.5 \\ 4.7 & 5.4 & 1.0 & -70.7 & 450.0 & 89.7 & -2.5 \\ -15.1 & 8.3 & -8.1 & -14.7 & 89.7 & 330.0 & 32.7 \\ -7.8 & 0.8 & 5.1 & -61.5 & -2.5 & 32.7 & 280.0 \end{pmatrix}$$

Site basis

Deconstructing the dynamics

Opinion: This is obvious

$$H=\begin{pmatrix} 215 & -104.1 & 5.1 & -4.3 & 4.7 & -15.1 & -7.8 \\ -104.1 & 220.0 & 32.6 & 7.1 & 5.4 & 8.3 & 0.8 \\ 5.1 & 32.6 & 0.0 & -46.8 & 1.0 & -8.1 & 5.1 \\ -4.3 & 7.1 & -46.8 & 125.0 & -70.7 & -14.7 & -61.5 \\ 4.7 & 5.4 & 1.0 & -70.7 & 450.0 & 89.7 & -2.5 \\ -15.1 & 8.3 & -8.1 & -14.7 & 89.7 & 330.0 & 32.7 \\ -7.8 & 0.8 & 5.1 & -61.5 & -2.5 & 32.7 & 280.0 \end{pmatrix}$$

$$H=\begin{pmatrix} 513 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 332 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 307 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 268 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 121 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 102 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -23 \end{pmatrix}$$

Site basis

Exciton basis

$\Downarrow$

No coherent dynamics left

$\Downarrow$

Noise supports transport

Deconstructing the transport dynamics

Opinion: This is obvious

$$H=\begin{pmatrix} 215 & -104.1 & 5.1 & -4.3 & 4.7 & -15.1 & -7.8 \\ -104.1 & 220.0 & 32.6 & 7.1 & 5.4 & 8.3 & 0.8 \\ 5.1 & 32.6 & 0.0 & -46.8 & 1.0 & -8.1 & 5.1 \\ -4.3 & 7.1 & -46.8 & 125.0 & -70.7 & -14.7 & -61.5 \\ 4.7 & 5.4 & 1.0 & -70.7 & 450.0 & 89.7 & -2.5 \\ -15.1 & 8.3 & -8.1 & -14.7 & 89.7 & 330.0 & 32.7 \\ -7.8 & 0.8 & 5.1 & -61.5 & -2.5 & 32.7 & 280.0 \end{pmatrix}$$

Site basis

$$H=\begin{pmatrix} 513 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 332 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 307 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 268 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 121 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 102 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -23 \end{pmatrix}$$

Exciton basis

$\Downarrow$

No coherent dynamics left

$\Downarrow$

Noise supports transport

But: Answer depends on structure of network

Sometimes noise helps
sometimes it hinders transport

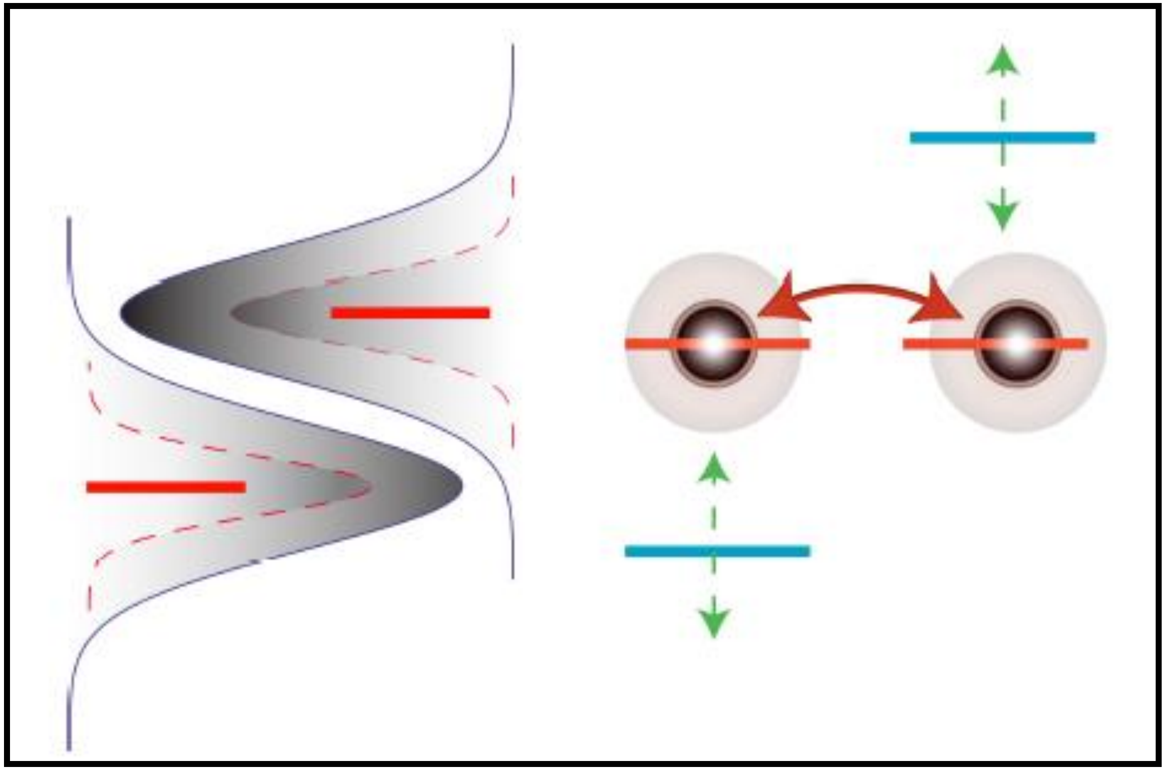
Moreover: Is exciton relaxation entirely incoherent?

How can *noise* assist transport?

Identifying the building blocks for NAT (noise assisted transport) (or ENAQT (environment assisted quantum transport))

Basic Mechanisms underpinning noise assisted transport

(1) Bridging energy gaps and blocking unfavourable (coherent) transport paths



Typical **line broadening** mechanisms
Excess noise may not always be detrimental

Basic Mechanisms underpinning noise assisted transport

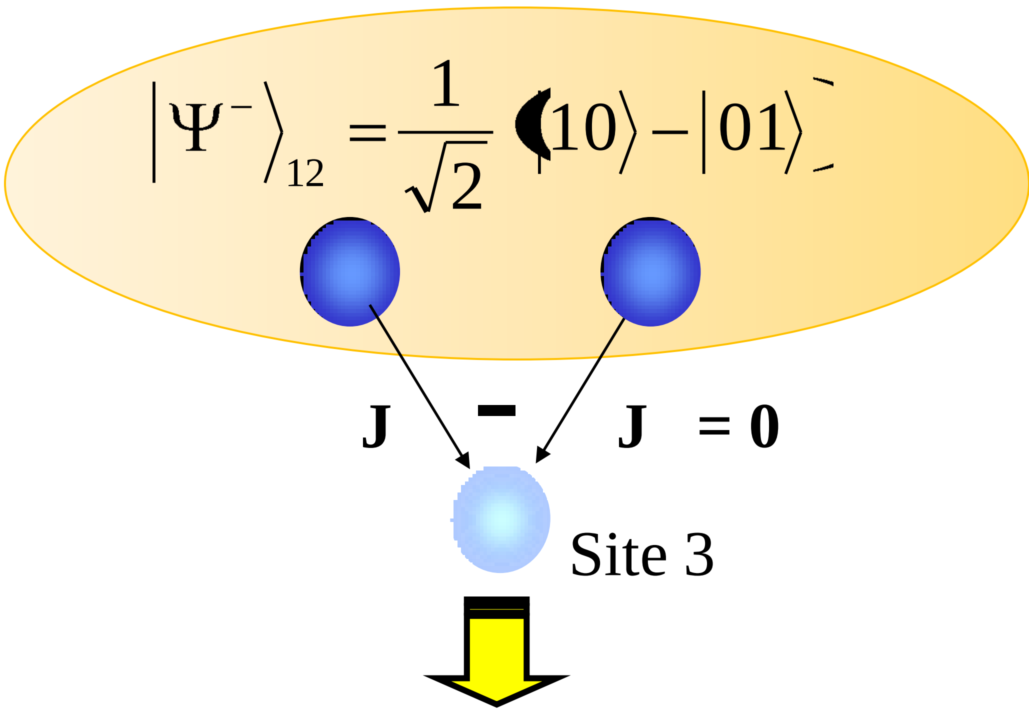
(2) Interference effects

Simplest case: N=3 network

$$H = \sum_{k=1}^{3} E_i |i\rangle\langle i| + \sum_{k=1}^{2} J_{k3}(|k\rangle\langle 3| + h.c)$$

$$J_{13} = J_{23}$$

Destructive interference of tunneling amplitudes.
Transport to site 3 is inhibited

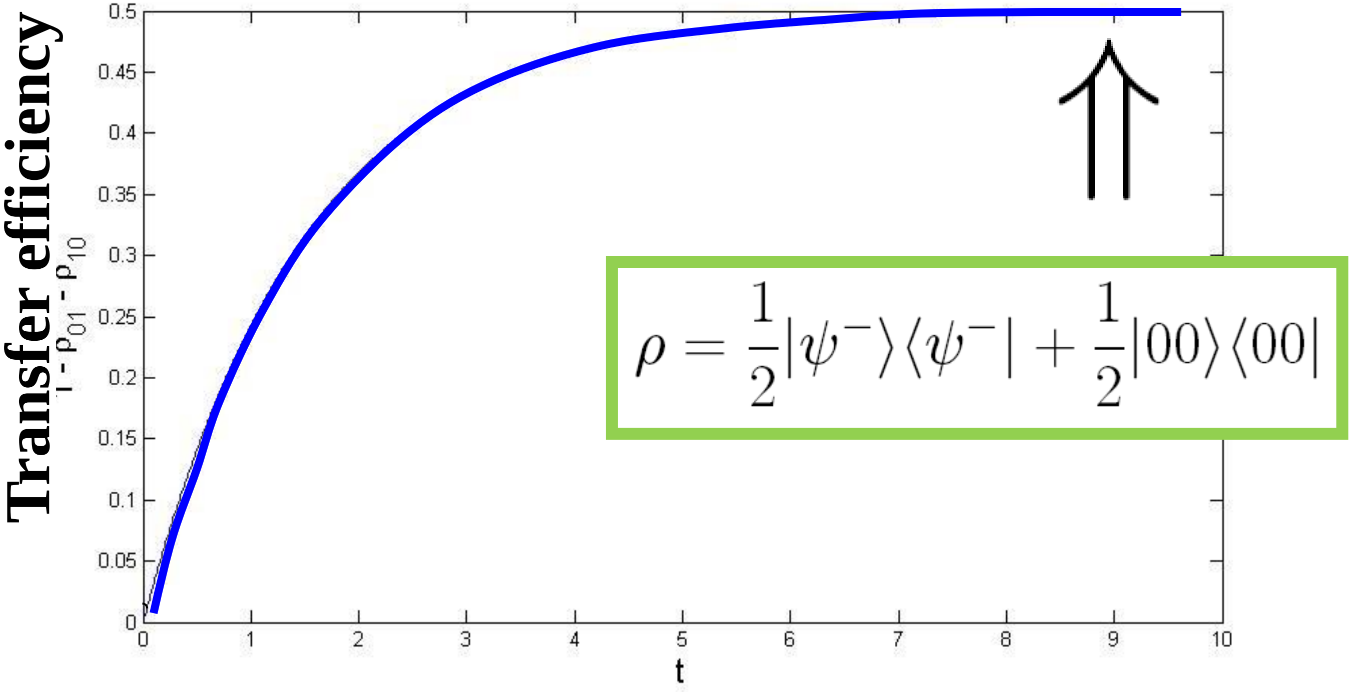


Trapping site

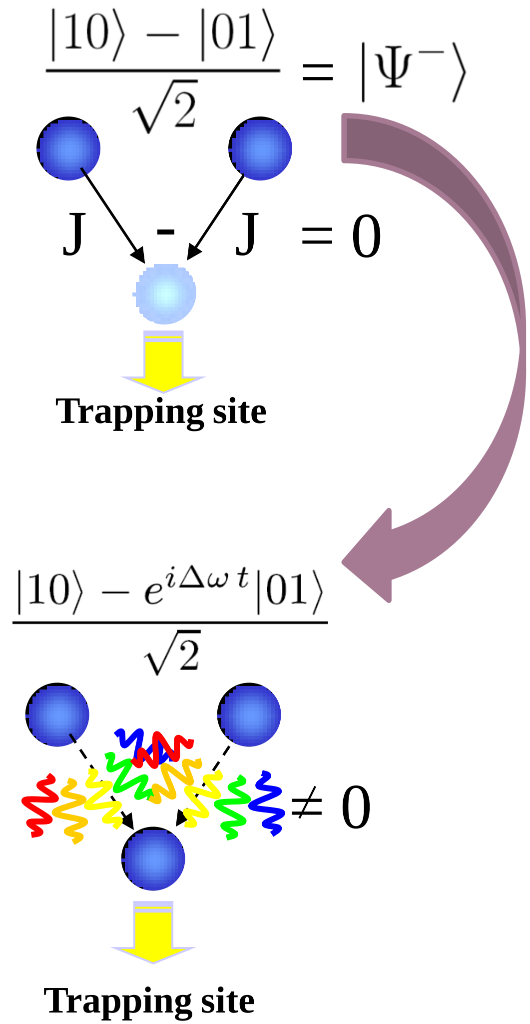
(2) Interference effects

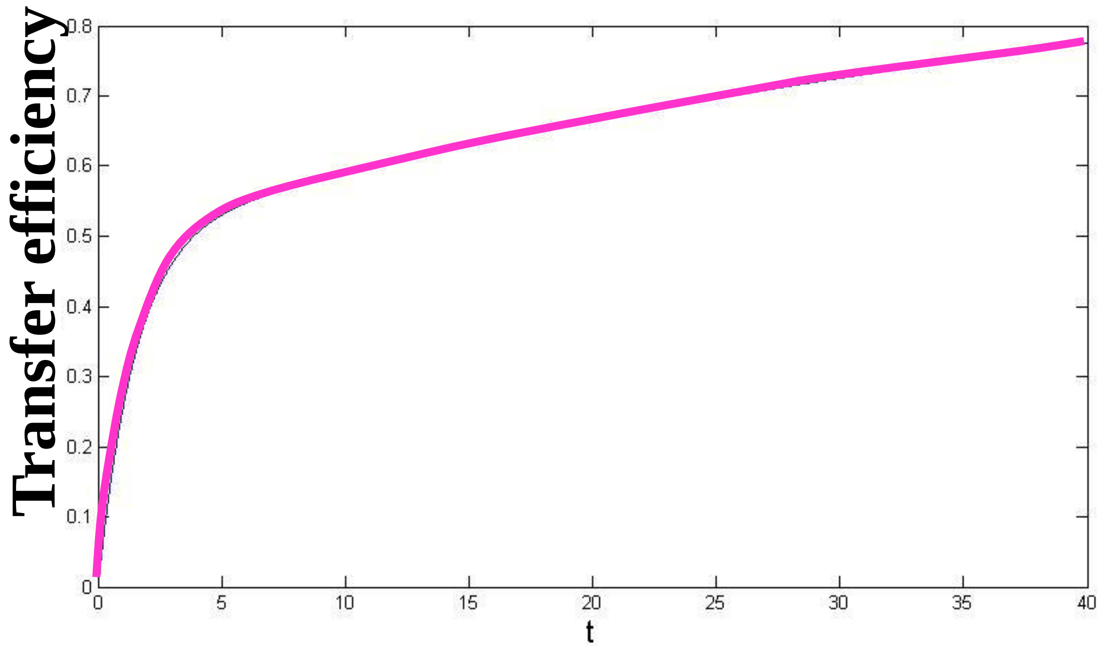
Selective excitation:

$$|01\rangle = \frac{1}{\sqrt{2}}\left[\frac{|01\rangle - |10\rangle}{\sqrt{2}} + \frac{|01\rangle + |10\rangle}{\sqrt{2}}\right]$$



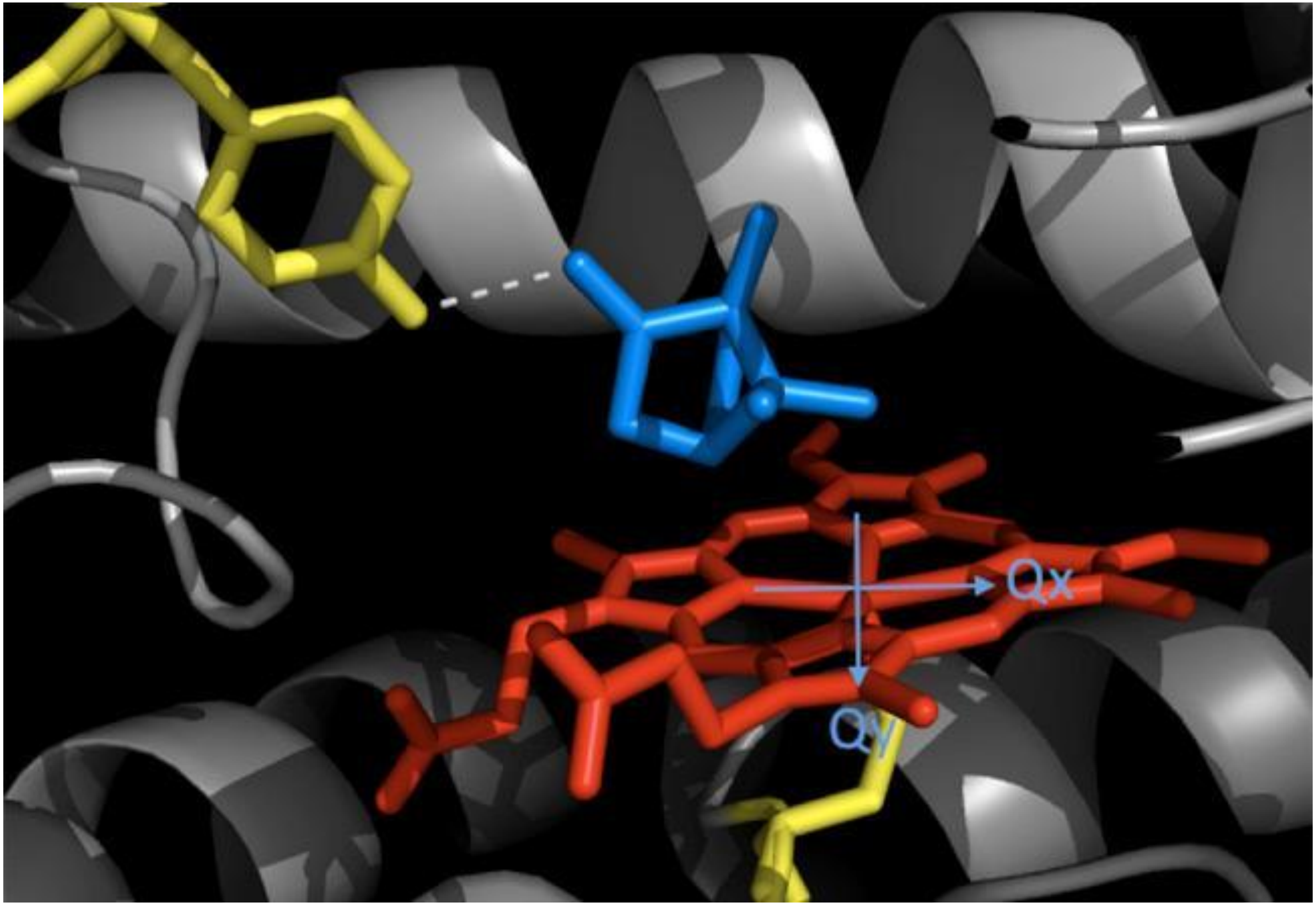
What effects can release a non-propagating state ?





Reduction of destructive interference effects → Transport

Is this relevant in the context of EET?

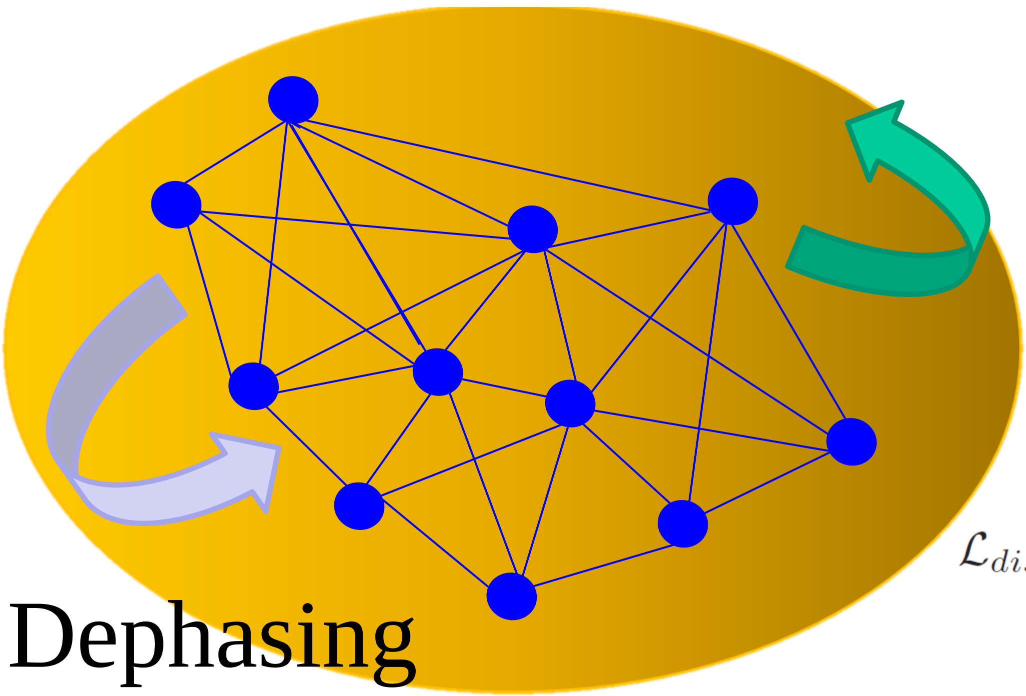


Dominant noise source: Pure dephasing due to protein environment

Simplest Theoretical Model

$$\frac{d\rho}{dt} = -i[H,\rho] + \mathcal{L}_{deph}(\rho) + \mathcal{L}_{diss}(\rho)$$

$$H = \sum_{j=1}^{N} \hbar\omega_j \sigma_j^+\sigma_j^- + \sum_{j\neq l} \hbar v_{j,l}(\sigma_j^-\sigma_l^+ + \sigma_j^+\sigma_l^-)$$



Relaxation

Energy exchange

$$\mathcal{L}_{diss}(\rho) = \sum_{j=1}^{N} \Gamma_j[-\{\sigma_j^+\sigma_j^-,\rho\} + 2\sigma_j^-\rho\sigma_j^+]$$

(ps range)

Dephasing

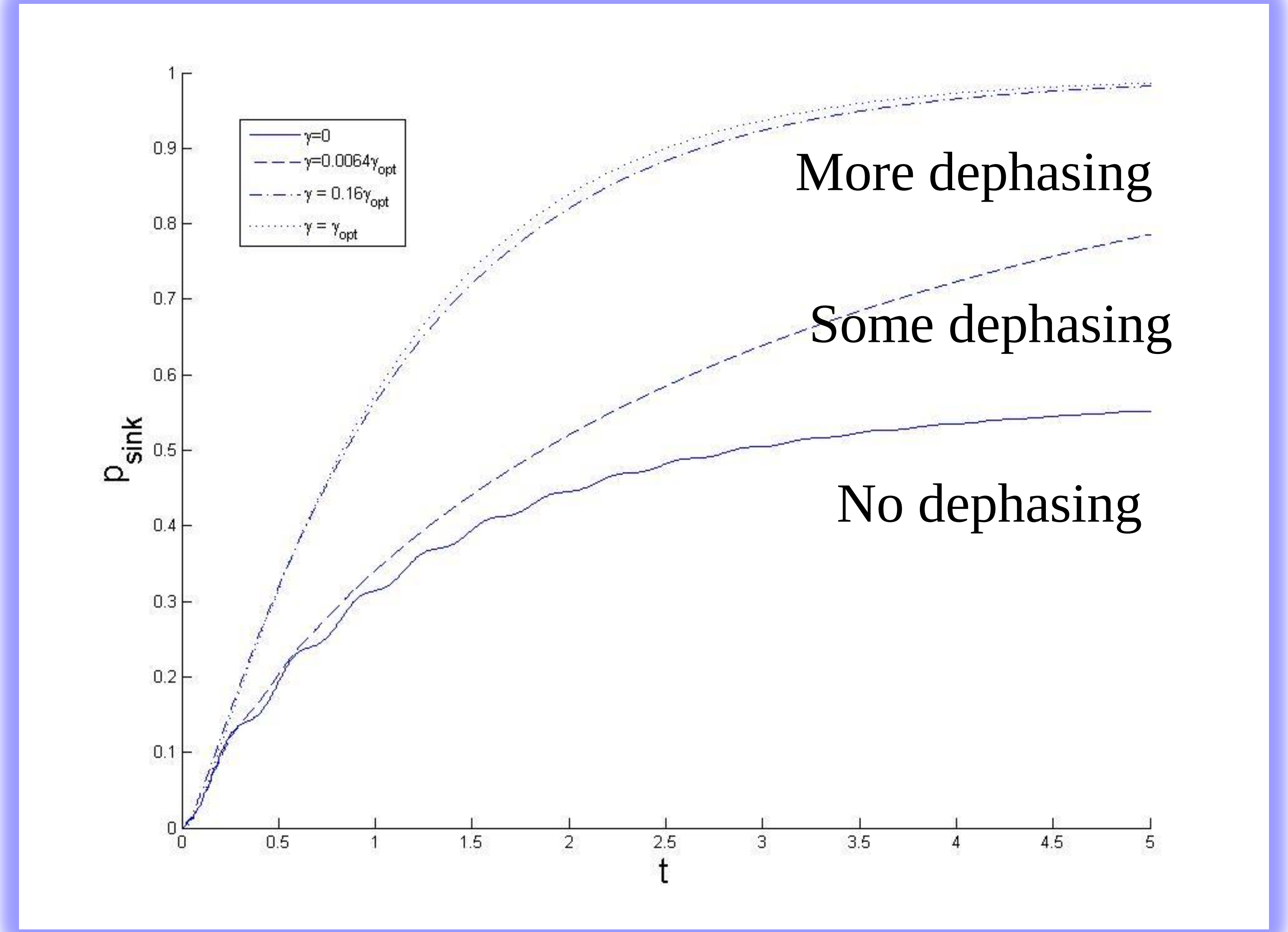
Phase randomization

$$\mathcal{L}_{deph}(\rho) = \sum_{j=1}^{N} \gamma_j[-\{\sigma_j^+\sigma_j^-,\rho\} + 2\sigma_j^+\sigma_j^-\rho\sigma_j^+\sigma_j^-]$$

Faster time scale (fs)

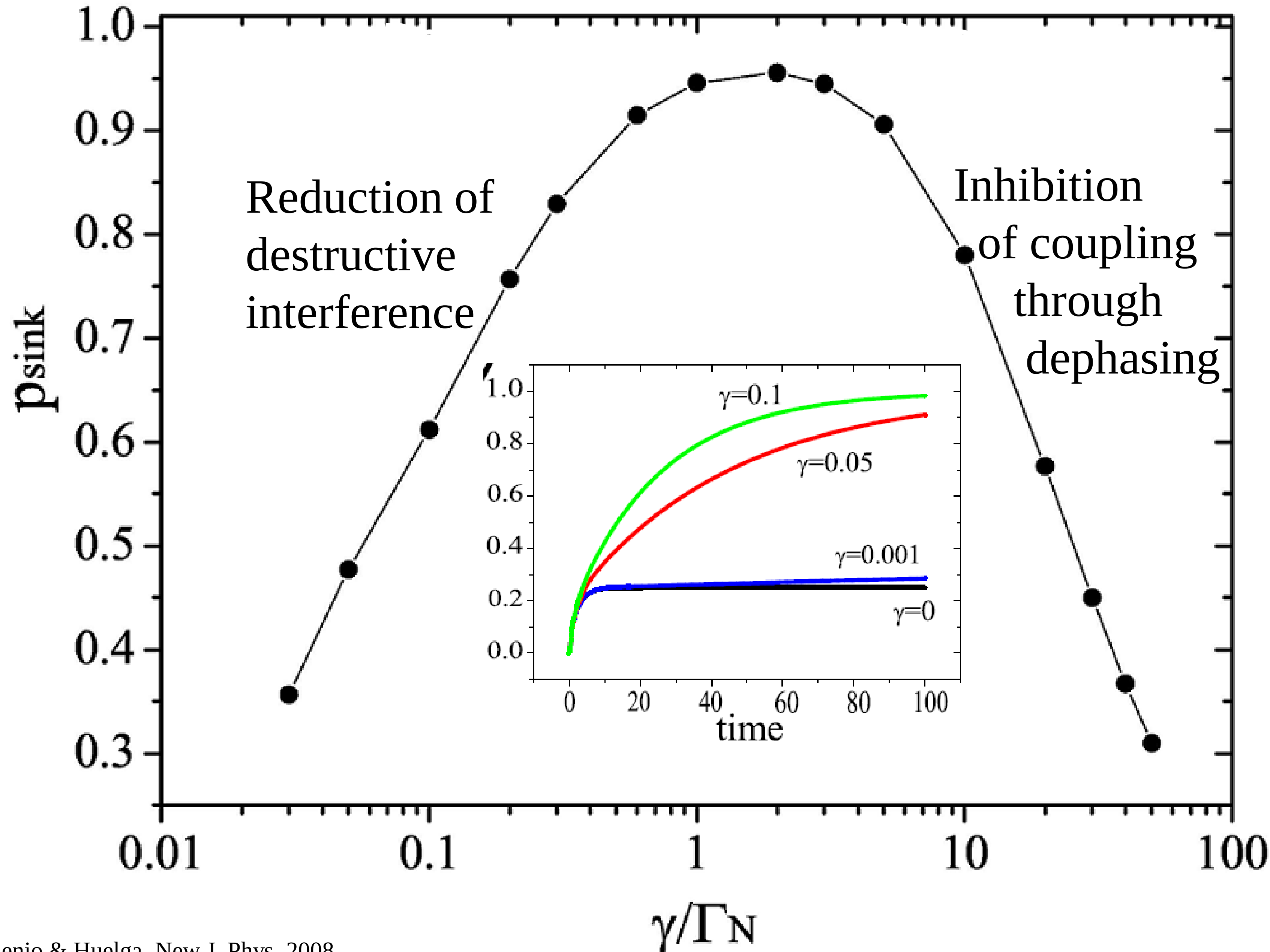
Dynamical Map is CPTP

Does it work for transport across FMO?



Plenio & Huelga, New J. Phys. 2008
Caruso, Chin, Datta, Huelga, Plenio, J. Chem. Phys. 2009
Chin, Caruso, Datta, Huelga, Plenio, New J. Phys. 2010

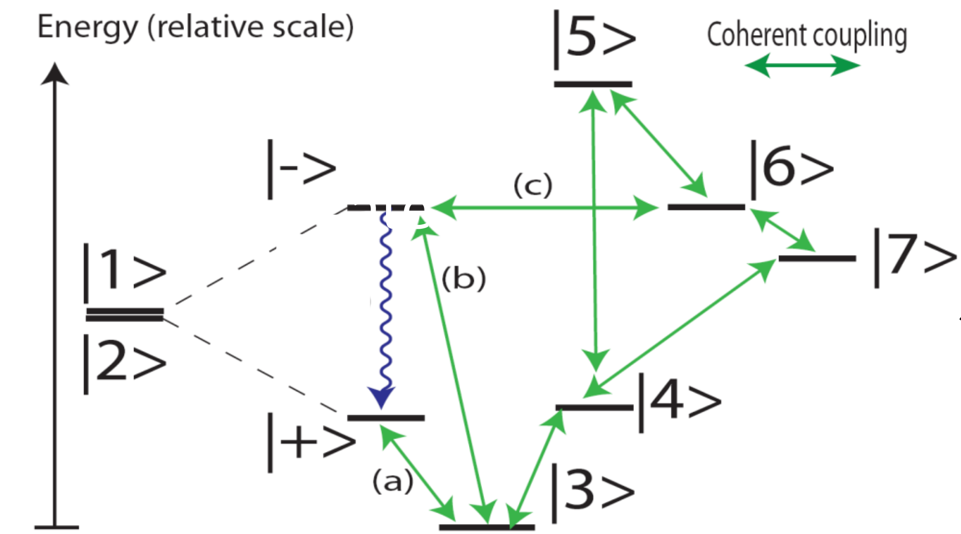
Mohseni, Rebentrost, Lloyd, Aspuru-Guzik, J. Phys. Chem. 2008
Rebentrost, Mohseni, Kassal, Lloyd, Aspuru-Guzik, New J. Phys. 2009



Plenio & Huelga, New J. Phys. 2008
Caruso, Chin, Datta, Huelga, Plenio, J. Chem. Phys. 2009
Chin, Caruso, Datta, Huelga, Plenio, New J. Phys. 2010

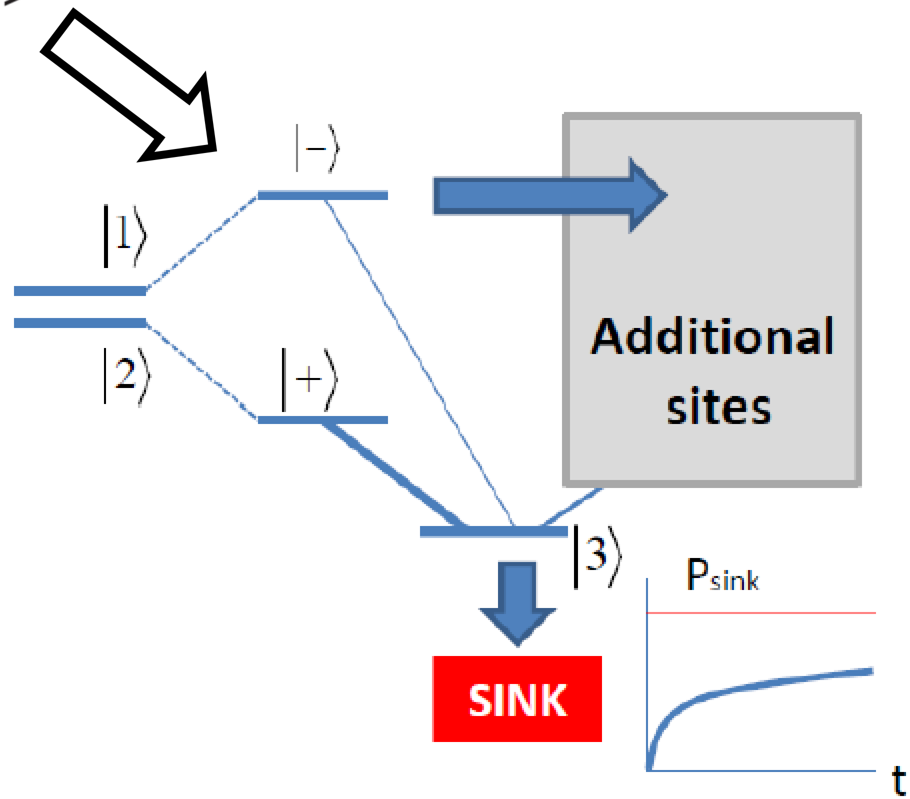
Mohseni, Rebentrost, Lloyd, Aspuru-Guzik, J. Phys. Chem. 2008
Rebentrost, Mohseni, Kassal, Lloyd, Aspuru-Guzik, New J. Phys. 2009

Transport dynamics in FMO
(microscopic details)

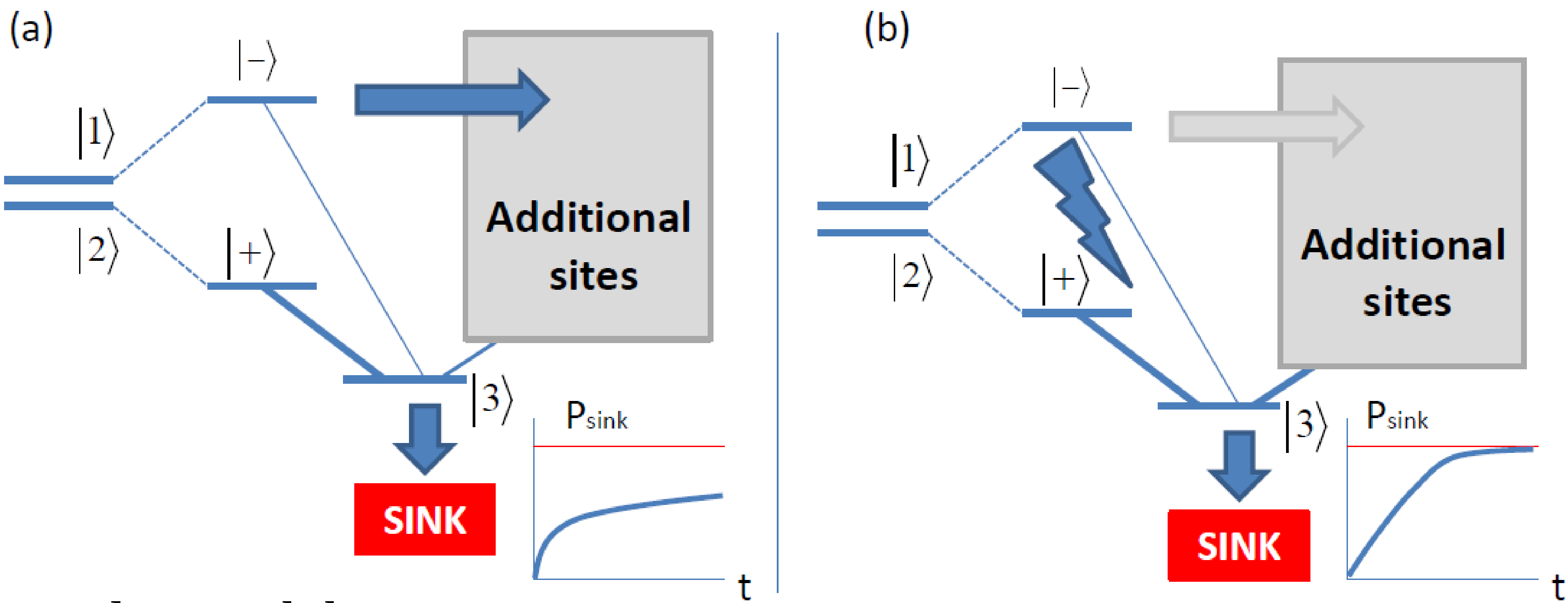


$\sqrt{2}|\pm\rangle = |1\rangle \pm |2\rangle$

Chin, Datta, Caruso, Huelga, Plenio, *NJP* **12**, 065002 (2010)



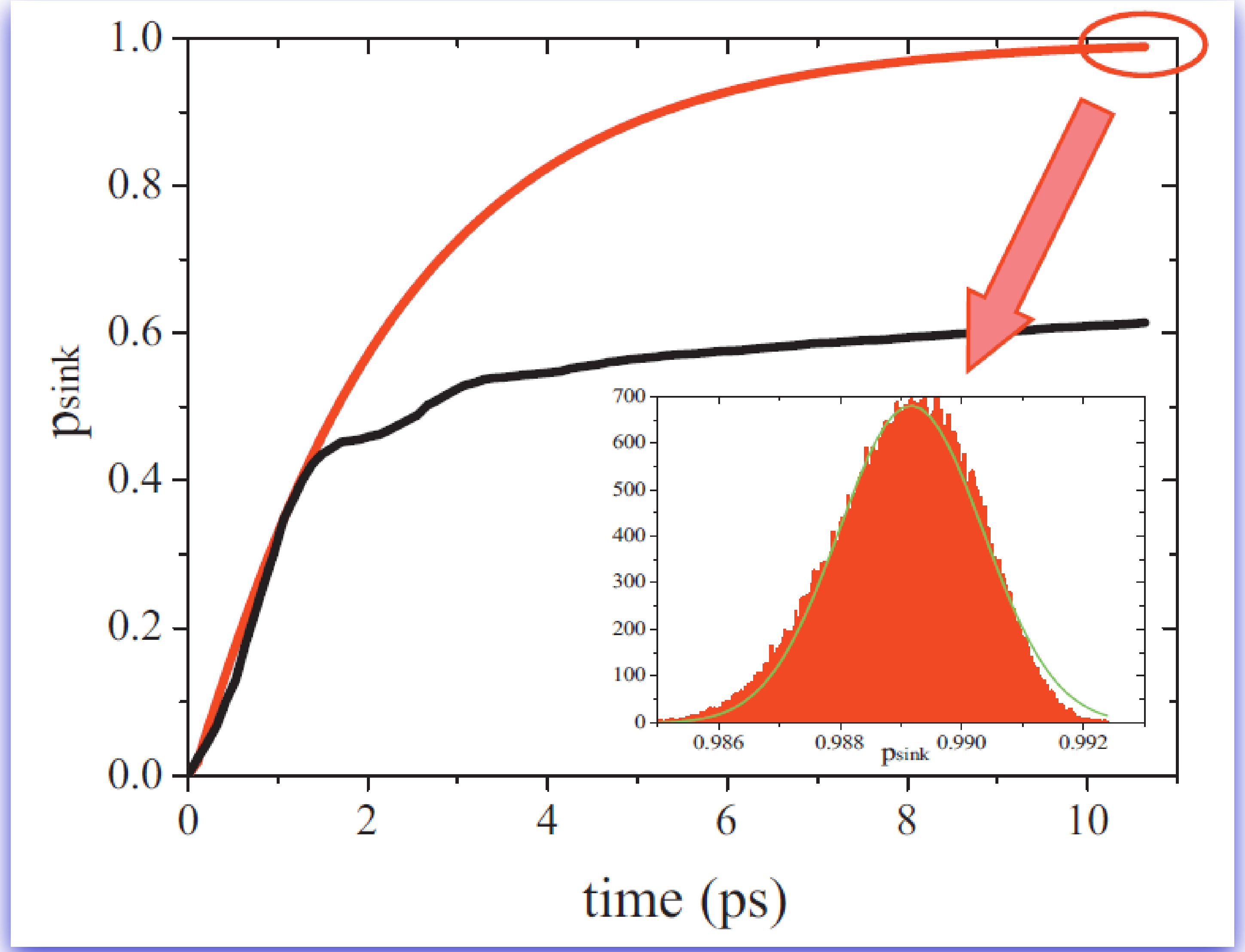
Transport dynamics in FMO
(microscopic details)



See also work by
Aspuru-Guzik et al
Ishizaki,Fleming et al
Whaley et al
Thorwart et al,....

Caruso, Chin, Datta, Huelga, Plenio, J Chem Phys 2009
Chin, Caruso, Datta, Huelga, Plenio, NJP 2010

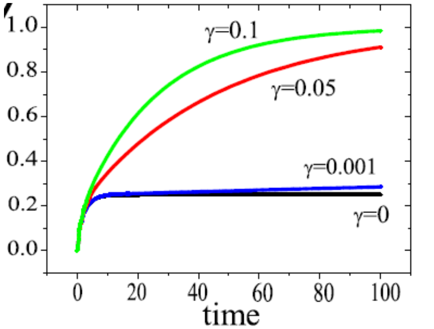
Robustness



Plenio & Huelga, New J. Phys. 2008
Caruso, Chin, Datta, Huelga, Plenio, J. Chem. Phys. 2009

Noise leads to the creation of transport paths that were forbidden under a purely quantum evolution

How?



Removal of destructive interference via dephasing of tunnelling amplitudes
Activation of energetically unfavourable transition via line broadening
Suppression of inefficient coherent paths

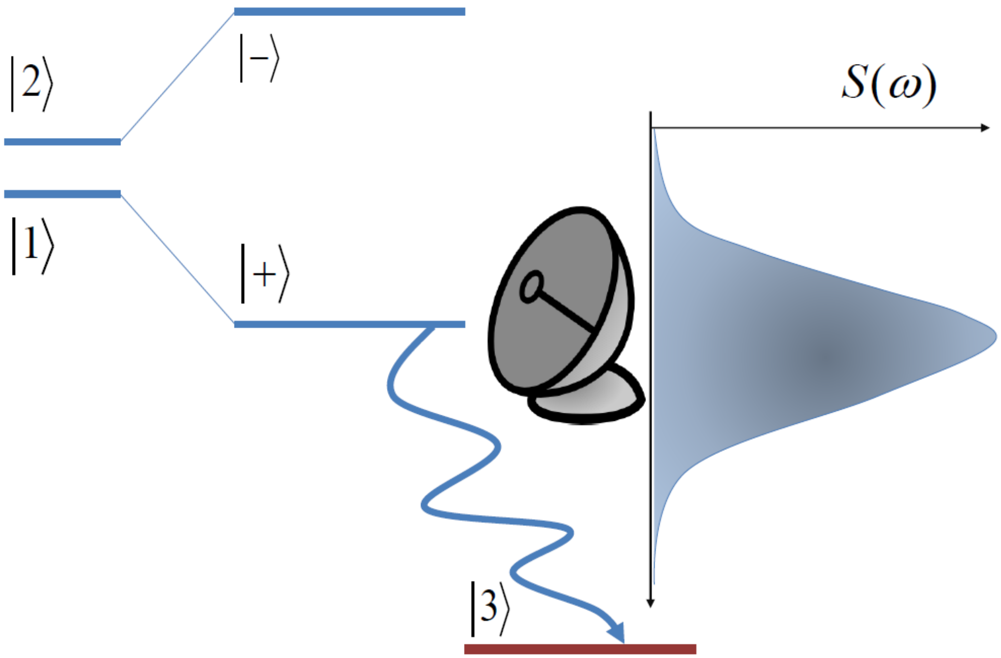
Moreover, the presence of coherent couplings can allow the system to efficiently harvest *noise* via the creation of a *phonon antennae*

Basic Mechanisms underpinning noise assisted transport

Possible structure in the environment has been ignored so far
Exciton relaxation may have a coherent component

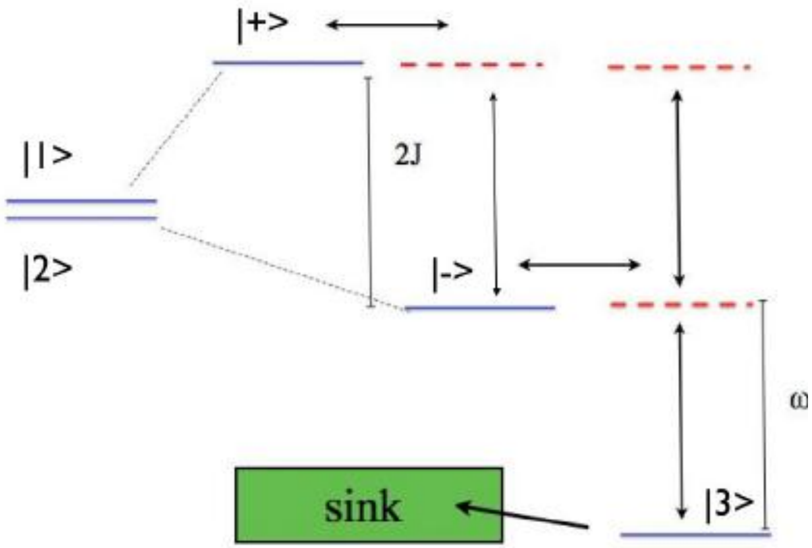
(3) Splitting of energy levels—Phonon Antennae

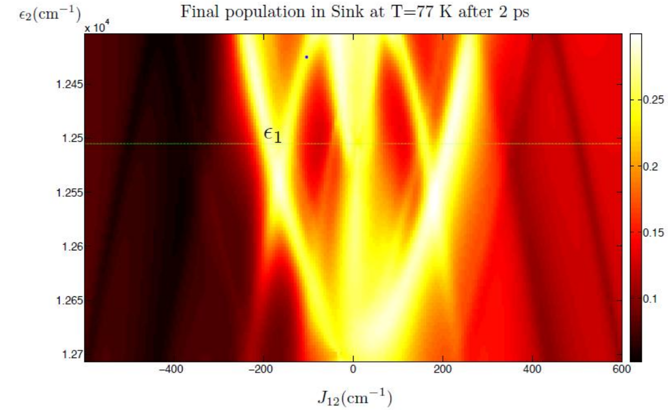
Electronic coupling may facilitate the creation of a **phonon antenna**

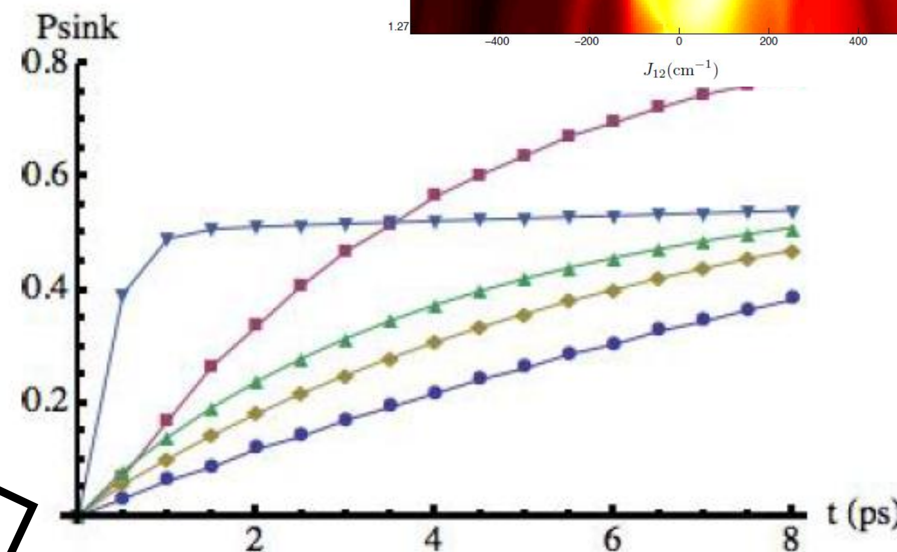


Chin, Huelga, Plenio, Phil.Trans.Royal Soc 2012
Eds. Olaya-Castro, Nazir & Fleming

(3) Splitting of energy levels—Phonon Antennae







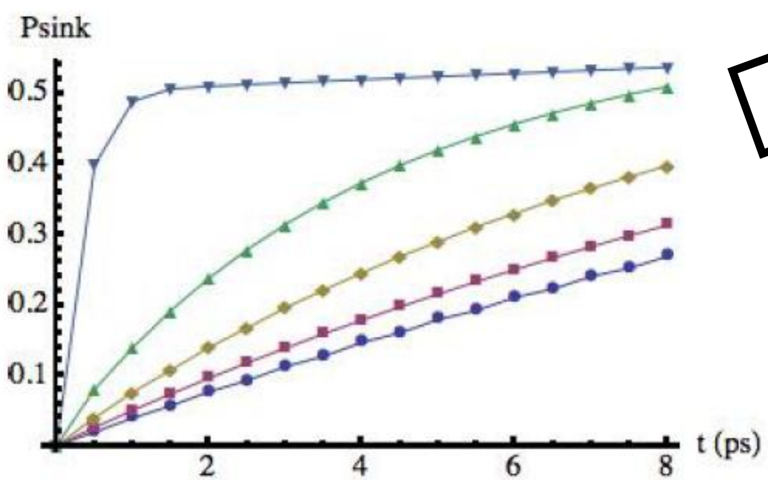
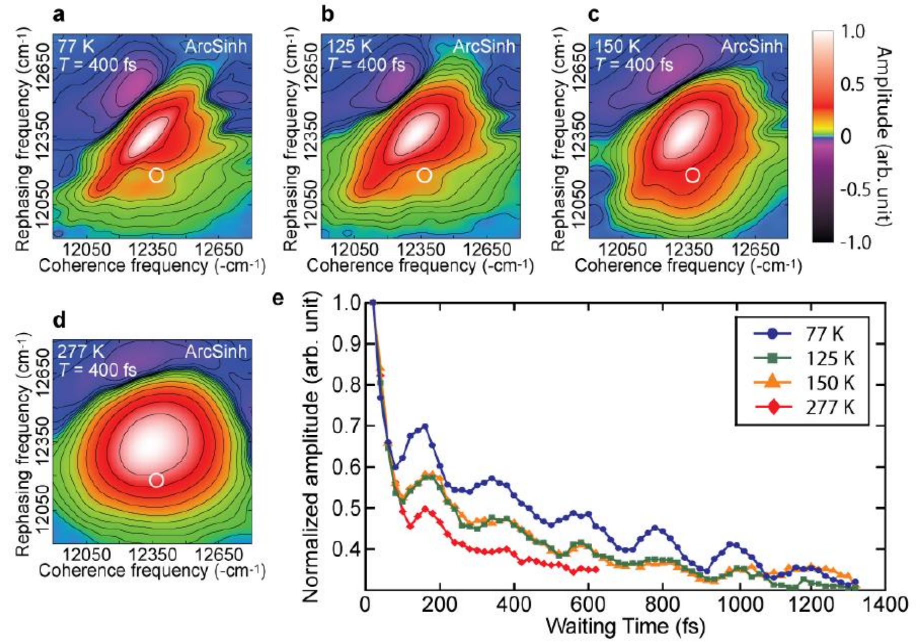


FIG. 6. *Psink* as a function of time for a three-site system without any coupling to a mode. Weak transport is now seen for $J_{12} = 100\text{cm}^{-1}$ (squares). the other curves are $J_{12} = 150\text{cm}^{-1}$ (diamonds),$J_{12} = 200\text{cm}^{-1}$ (triangles),$J_{12} = 300\text{cm}^{-1}$ (inverted squares) and $J_{12} = 50\text{cm}^{-1}$ (dots). For all curves $J_{23} = 30\text{cm}^{-1}$ and the initial state of the vibrational mode is a thermal state at 77 K.

Beyond transport

Engel et al, Science 2007
Panitchayangkoon et al, PNAS 2010

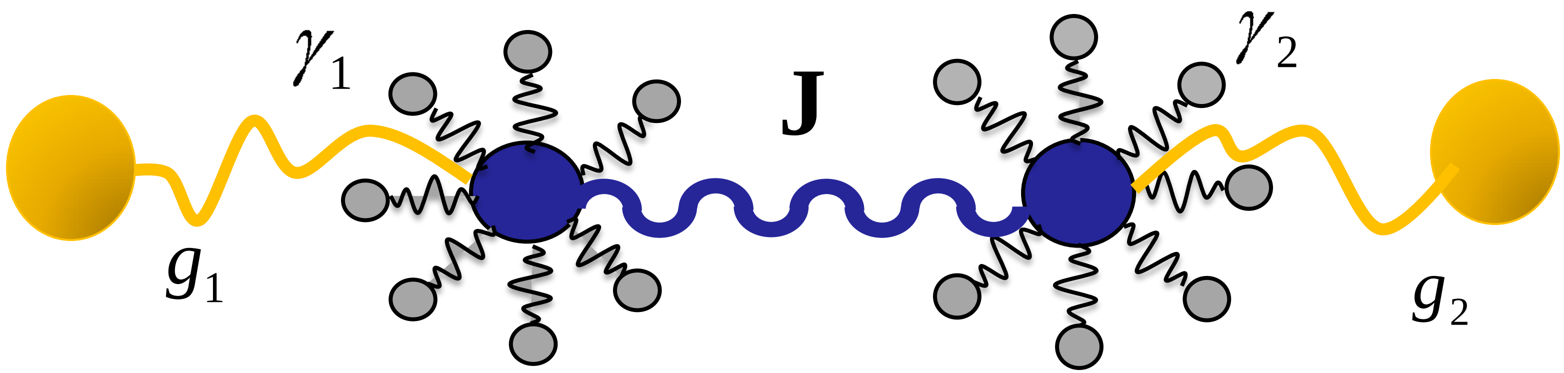


What about the *long lasting* coherences?

Experimental evidence from traditional spectroscopy supports the existence of localized vibrational modes (in particular modes quasiresonant with excitonic transitions)

Crucial??

Dimer system subject to the action of damped local modes



$$H = \sum_{j=1}^{2} \omega_j \sigma_j^+ \sigma_j^- + J(\sigma_1^- \sigma_2^+ + \sigma_1^+ \sigma_2^-)$$

γ_2

$$H_{s-m} = g_j \sigma_z^j (a_j + a_j^\dagger)$$

$$\mathcal{L}_{deph}(\rho) = \sum_{j=1}^{N} \gamma_j [-\{\sigma_j^+ \sigma_j^-, \rho\} + 2\sigma_j^+ \sigma_j^- \rho \sigma_j^+ \sigma_j^-]$$

System experiences **dephasing in the site basis**

Populations are preserved

Exciton versus site coherence

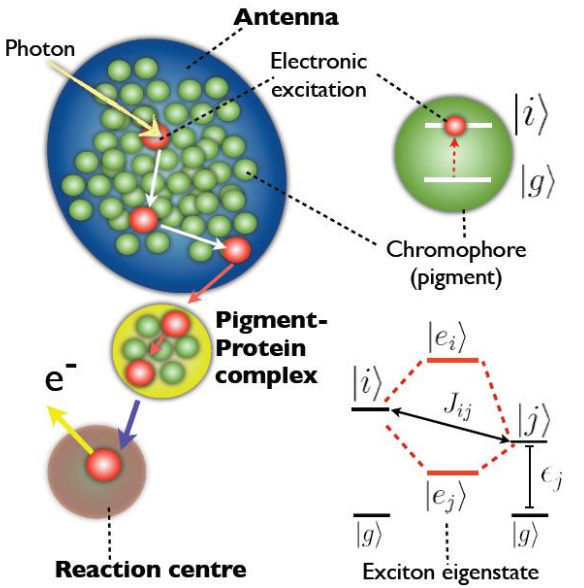
$$H = \sum_i \left((\epsilon_i + X_i)|i\rangle\langle i| + H_i^B \right) + \sum_{i \neq j} J_{ij}|i\rangle\langle j|$$

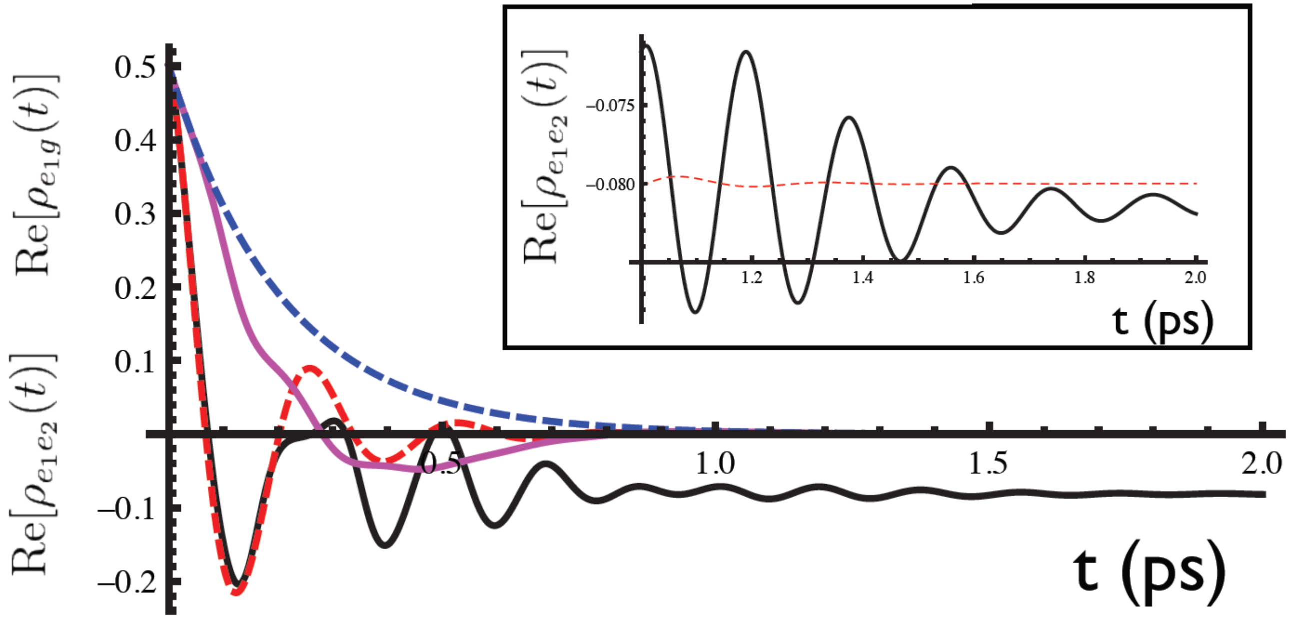
$$X_i = \sum_k g_{ik}(a_{ik} + a_{ik}^\dagger)$$

$$H_I = \frac{1}{2}\sum_{n,m}(Q_{nm}|e_n\rangle\langle e_m| + h.c.),$$

$$Q_{nm} = \sum_{ik}\sqrt{S_k}\omega_k C_n^i C_m^i (a_{ik} + a_{ik}^\dagger)$$

$$H_{driving} \approx \frac{1}{2}\sum_{n \neq m}(\langle Q_{nm}\rangle(t)|e_n\rangle\langle e_m| + h.c.)$$





Semiclassical

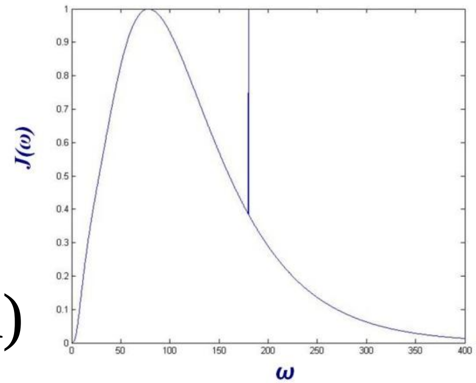
Chin, Prior, Rosenbach, Caycedo, Huelga, Plenio, arXiv 1203.0776

Towards a realistic description of long lasting coherence

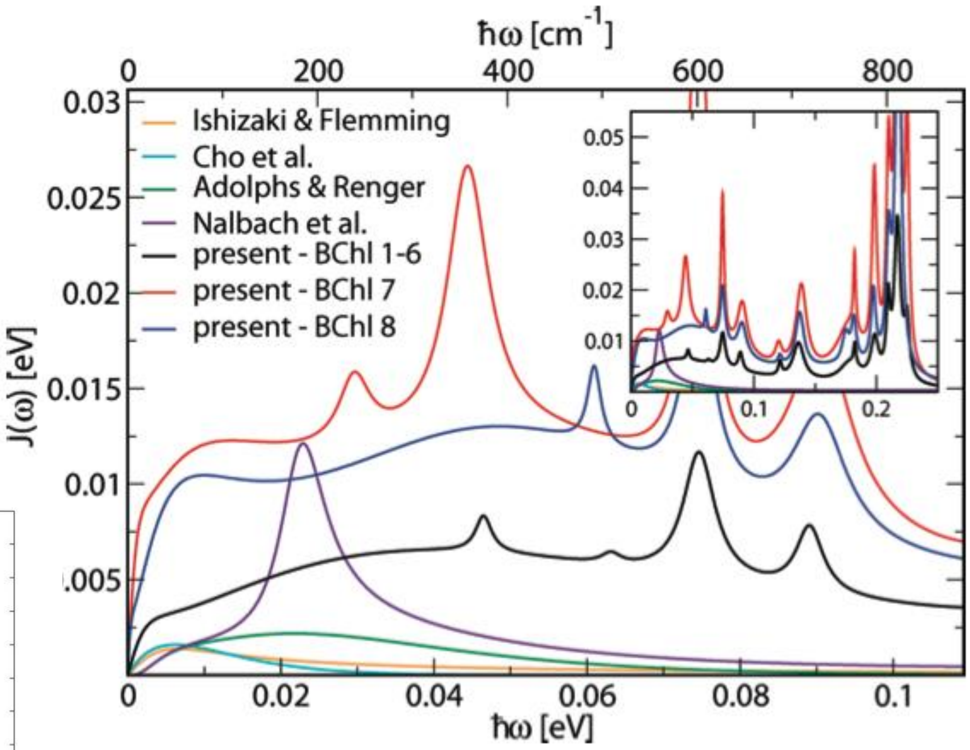
Standard open system theory inappropriate for pigment-protein complexes

-Slow fluctuations, long memory
Non-Markovian dynamics

-Strong couplings and spatial correlation
-Structured spectral function
non-perturbative



(AR)



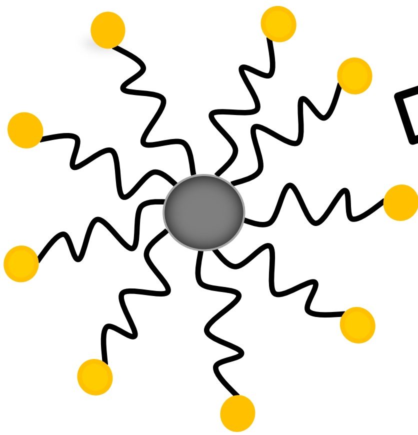
Olbrich et al. J. Phys. Chem Lett. 2. 2011

Significantly correlated system-bath dynamics –Many-body physics important

Efficient exact simulation of many body systems (TEDOPA)

Main result: Powerful numerical tool with associated physical insight

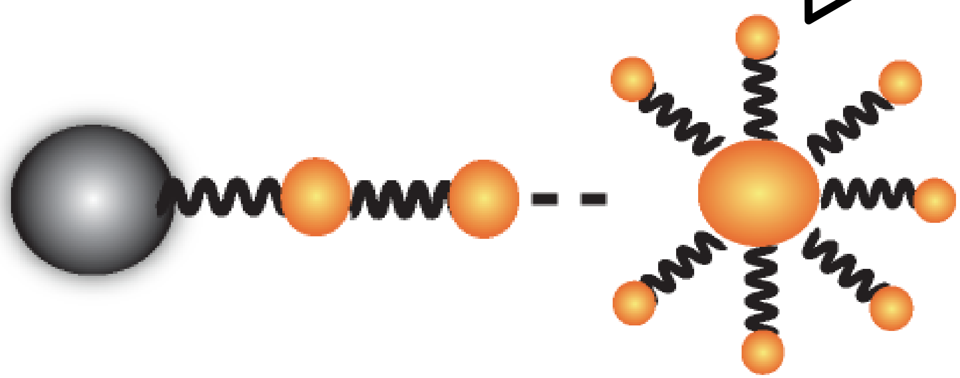
J. Prior, A. Chin, SH and MB Plenio,
Efficient simulation of strong system-environment interactions,
Phys. Rev. Lett. **105**, 050404 (2010)



Unitary transformation of bosonic modes

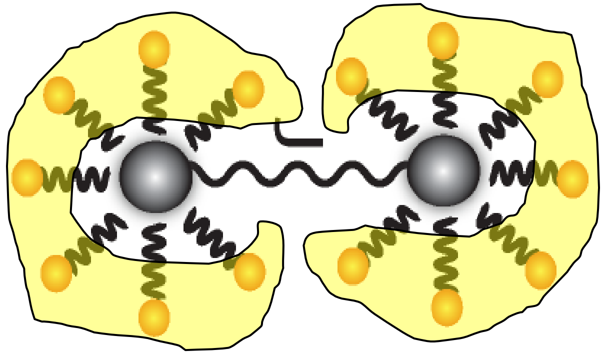
Universal features

New – **Analytical mapping, avoids previous numerical instabilities**



Non-perturbative description of system-environment interaction for structured environments

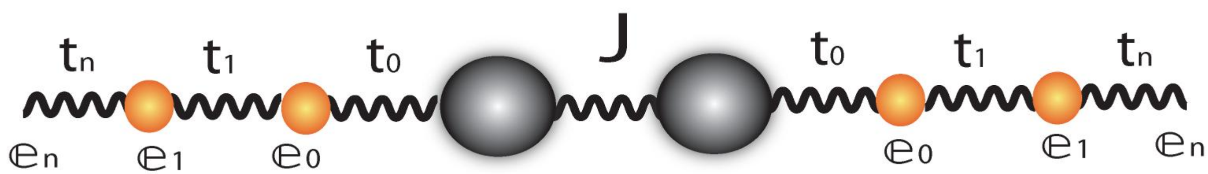
$$H_{res} = \int dx\, g(x) a_x^\dagger a_x$$



$$V = \int dx\, h(x) \hat{A}(a_x^\dagger + a_x)$$

$$b_n^\dagger = \int dx\, U_n(x) a_x^\dagger$$

Exact, thanks to theory of orthonormal polynomials

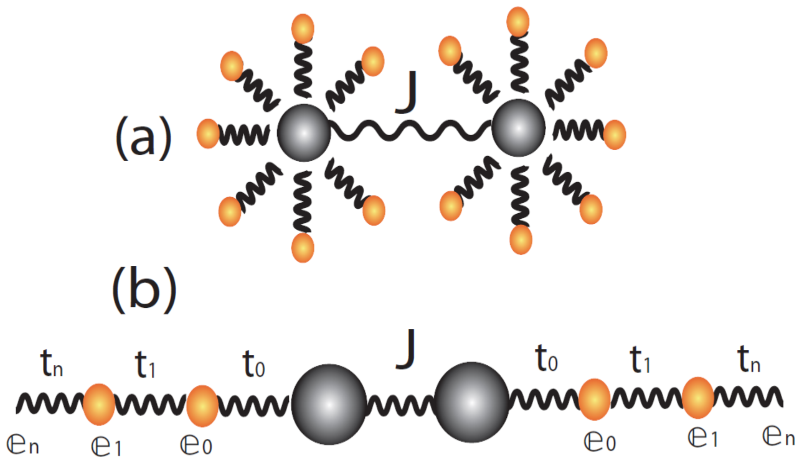


t-DMRG yields dynamics for general spectral densities

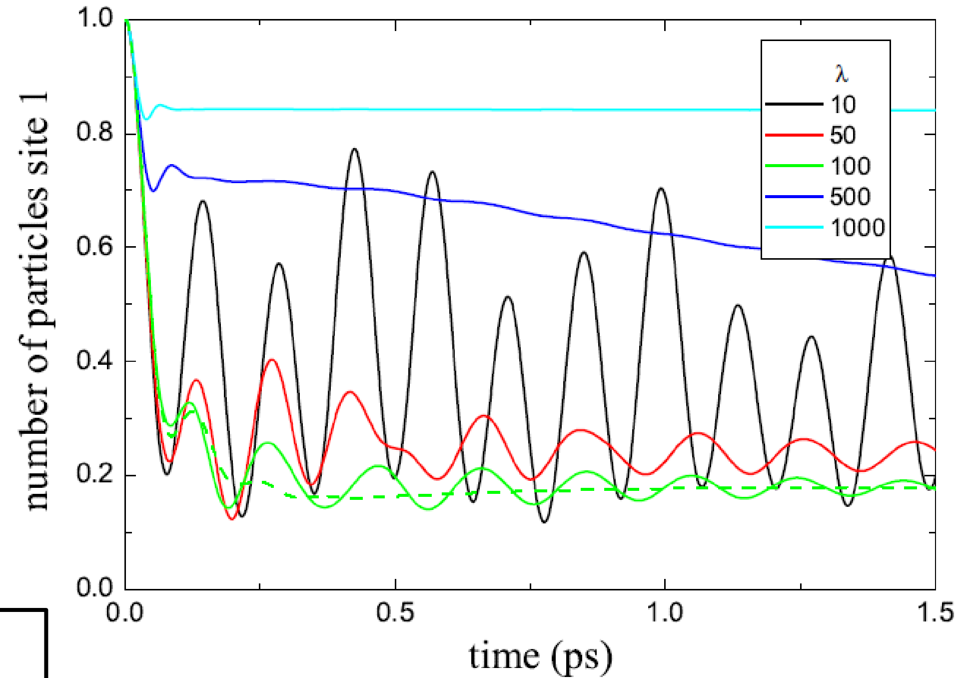
$$c_0 \hat{A}(b_0 + b_0^\dagger) + \sum_{n=0}^{\infty} \omega_n b_n^\dagger b_n + t_n b_{n+1}^\dagger b_n + t_n b_n^\dagger b_{n+1}$$

J. Math. Phys. **51**, 092109 (2010)

Efficient simulation of strong system-environment interactions: dimer system (building block of complex bio-molecular aggregates)



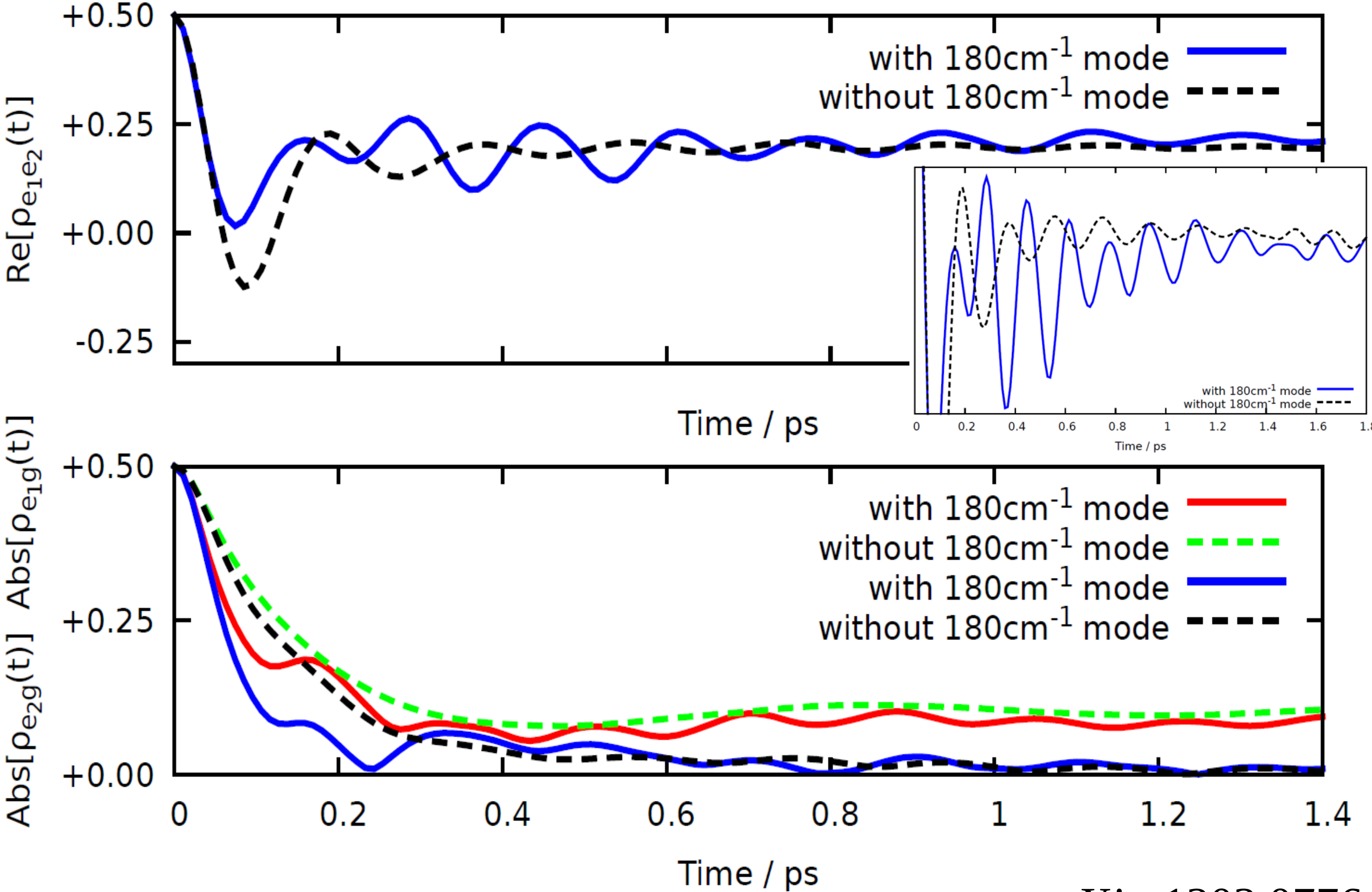
$$J(\omega) = \frac{2\pi\lambda\left[1000\omega^5 e^{-\left(\frac{\omega}{\omega_1}\right)^{\frac{1}{2}}} + 4.3\omega^5 e^{-\left(\frac{\omega}{\omega_2}\right)^{\frac{1}{2}}}\right]}{9!(1000\omega_1^5 + 4.3\omega_2^5)} + 4\pi S_H \omega_H^2 \delta(\omega - \omega_H),$$



Can obtain good fits to
beating patterns as reported by Engel's group
(Hayes et al. NJP. 2. (2010);
Hayes et al. Faraday Disc. 150. (2011)

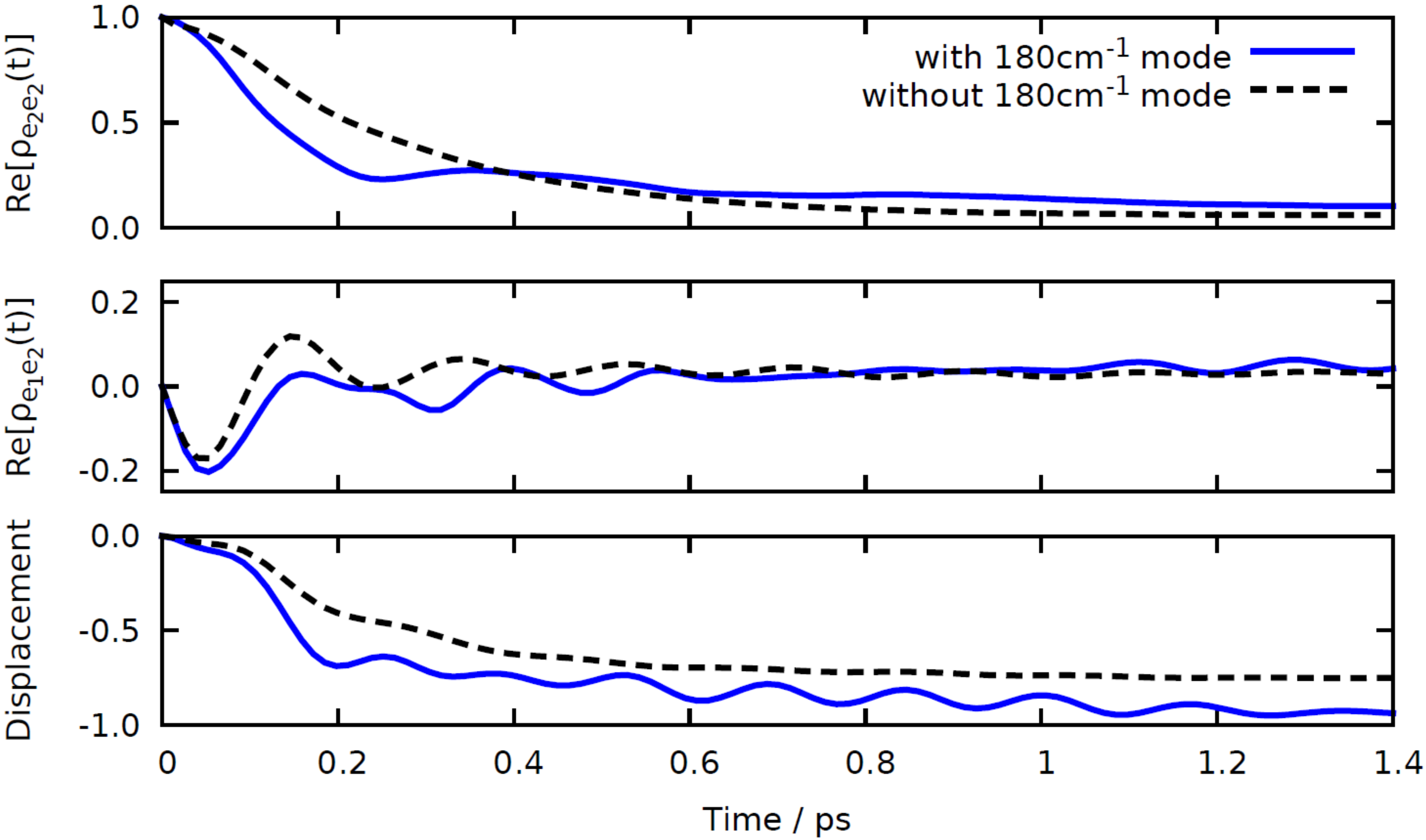
J. Prior, A. Chin, SH and MB Plenio,
Phys. Rev. Lett. **105**, 050404 (2010)

Exact Simulations (T=77 K)



arXiv:1203.0776

Exact Simulations



arXiv:1203.0776

Other results involving localized modes:
Mancal &Pullerits, Olaya-Castro & Scholes, Kreisbeck & Kramer **(arXiv 2012)**

Conclusions

- The basis for efficient and robust transport in the FMO complex is provided by an intricate interplay of environmental protein interactions and coherent pigment-pigment couplings

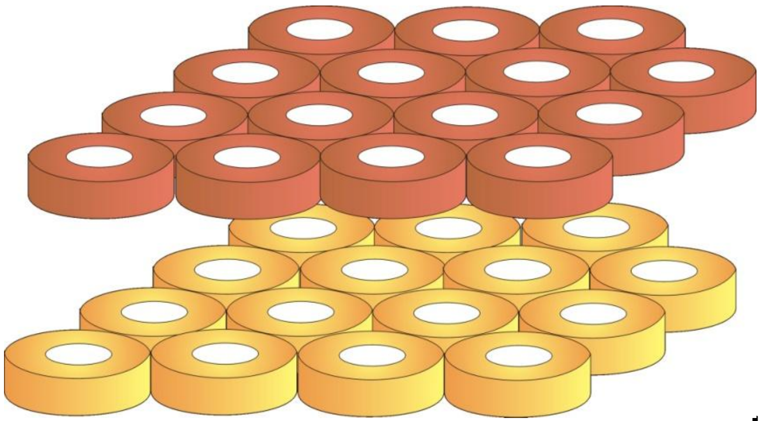
-Structure in the protein spectral density leads to strong coherent pigment-protein interactions –
boundary of *system* and *environment* is obscured.
Many-body treatment of open quantum dynamics needed

- Non-equilibirum system-bath (coherent) effects may be behind the enhancement of inter-exciton coherences

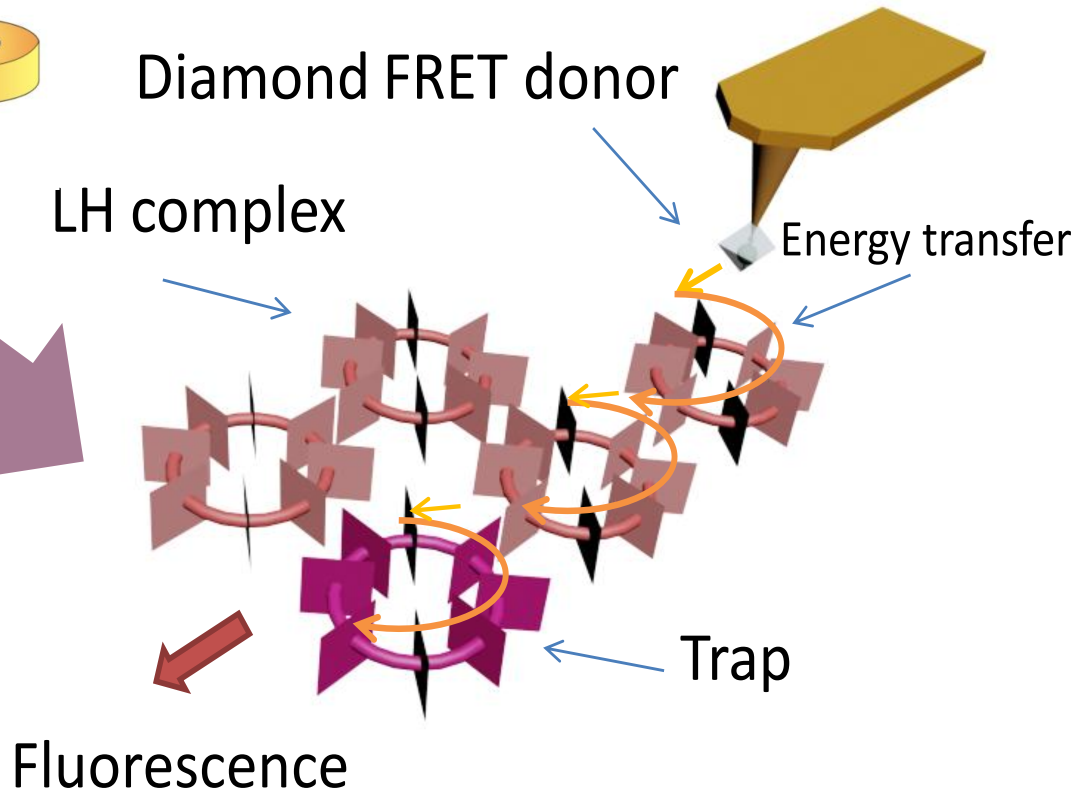
To do ....

- Simulate larger networks at finite temperature and with full structure
- Evaluation of spectral density from excitonically coupled systems (test bed WSCP)
- Compute 2D spectra from non-perturbative dynamics
- Extract clear dynamical features via different experimental techniques (quantum control)

What about the *big* question?



LH1 arrays
Scalable design
Controllable environment



Collaboration with Robin Gosh (Stuttgart) and Fedor Jelezko (Ulm)

Institut für Theorestische Physik

ulm university universität ulm

Permanent Staff
Martin Plenio
Susana Huelga
Dr Alex Retzker
Dr Ralf Aurich

Postdocs
Dr Javier Almeida
Dr Felipe Caycedo
Dr Marcus Cramer
Dr Shai Machnes
Dr Gor Nikoghosyan
Dr Abolfazal Bayat
Dr Alejandro Bermudez

PhD students
Mr Javier Cerrillo-Moreno
Mrs Clara Javaherian
Mr Ramil Nigmatullin
Mr Mischa Woods
Mr Andreas Albrecht
Mr Tillmann Baumgratz
Mr Robert Rosenbach
Mr Pablo de la Hoz

Academic Visitors
Dr Koenraad Audenaert
Dr Filippo Caruso (LENS, Florence)
Dr Alex Chin (DAMTP, Cambridge)
Dr Animesh Datta (Oxford)
Dr Javier Prior (Cartagena)
Mr Marco del Rey (CSIC, Madrid)

corner

PICC

Alexander von Humboldt
Stiftung/Foundation

Institut für Theorestische Physik

ulm university universität ulm

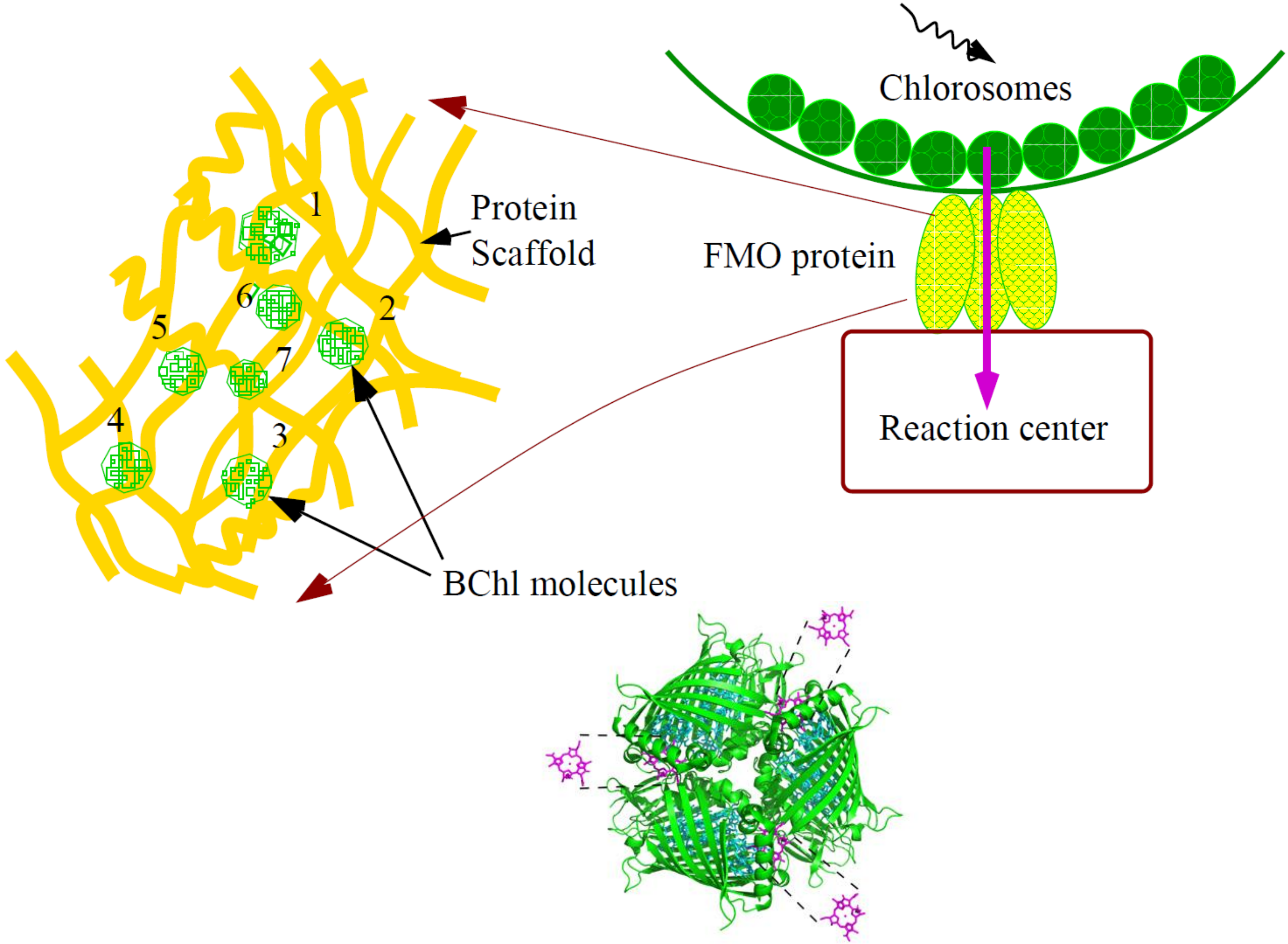
Main references from our group

New J. Phys. 10, 113019 (2008)
J. Chem. Phys. 131, 105106 (2009)
New J. Phys. 12 065002 (2010)
Phys. Rev. A 81, 062346 (2010)
Phys. Rev. Lett. 105, 050404 (2010)
Phys. Rev. Lett. 105, 190501 (2010)
J. Math. Phys. 51, 092109 (2010)
Procedia Chemistry 3, 248 (2011)
Phys. Rev. A 85, 042331 (2012)
J. Chem. Phys. 136, 155102 (2012)
arXiv:1203.5072
arXiv:1203.0776

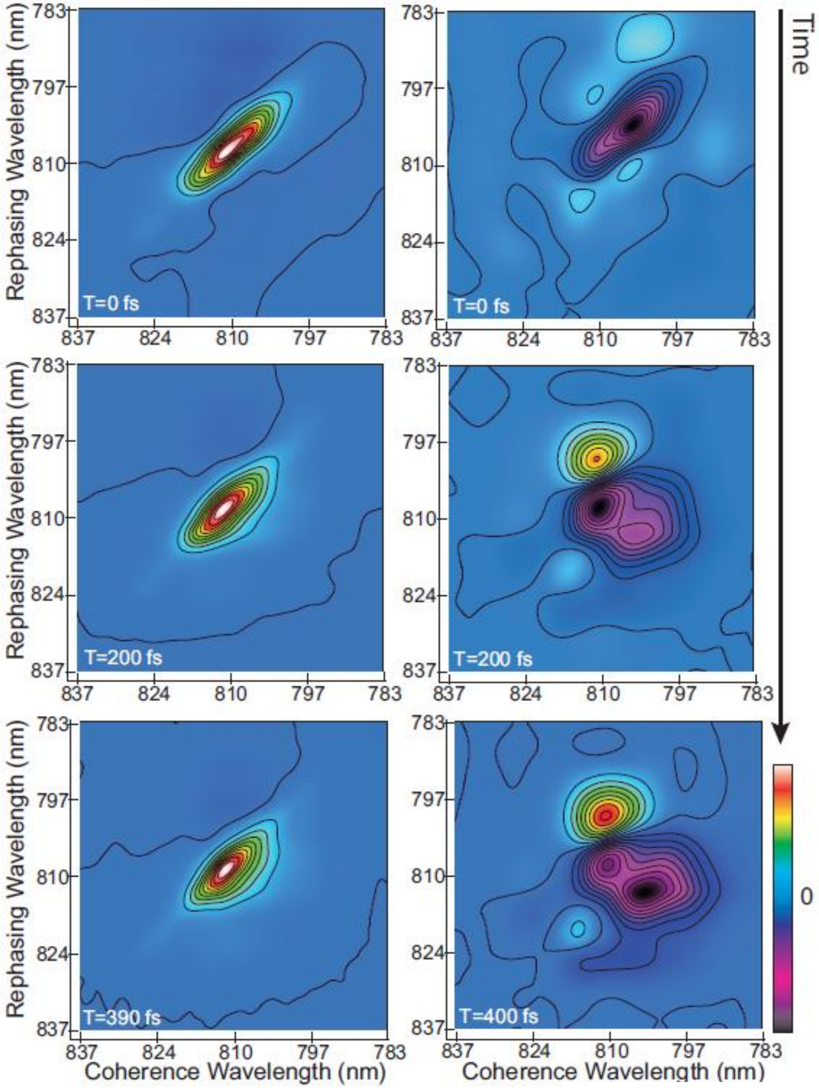
corner

PICC

Alexander von Humboldt
Stiftung / Foundation



Chlorosomes
Protein
Scaffold
FMO protein
Reaction center
BChl molecules
1
2
3
4
5
6
7



Cross-peak-specific two-dimensional electronic spectroscopy

Elizabeth L. Read[†‡], Gregory S. Engel[†‡], Tessa R. Calhoun[†‡], Tomáš Mančal[†‡§], Tae Kyu Ahn[†‡], Robert E. Blankenship[¶], and Graham R. Fleming[†‡‖]

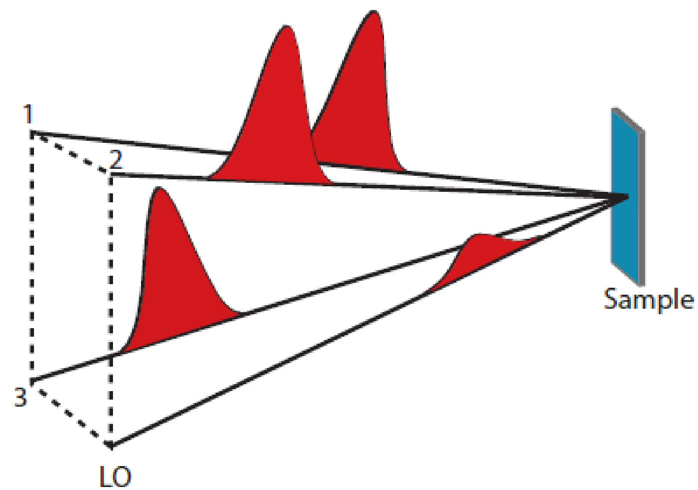
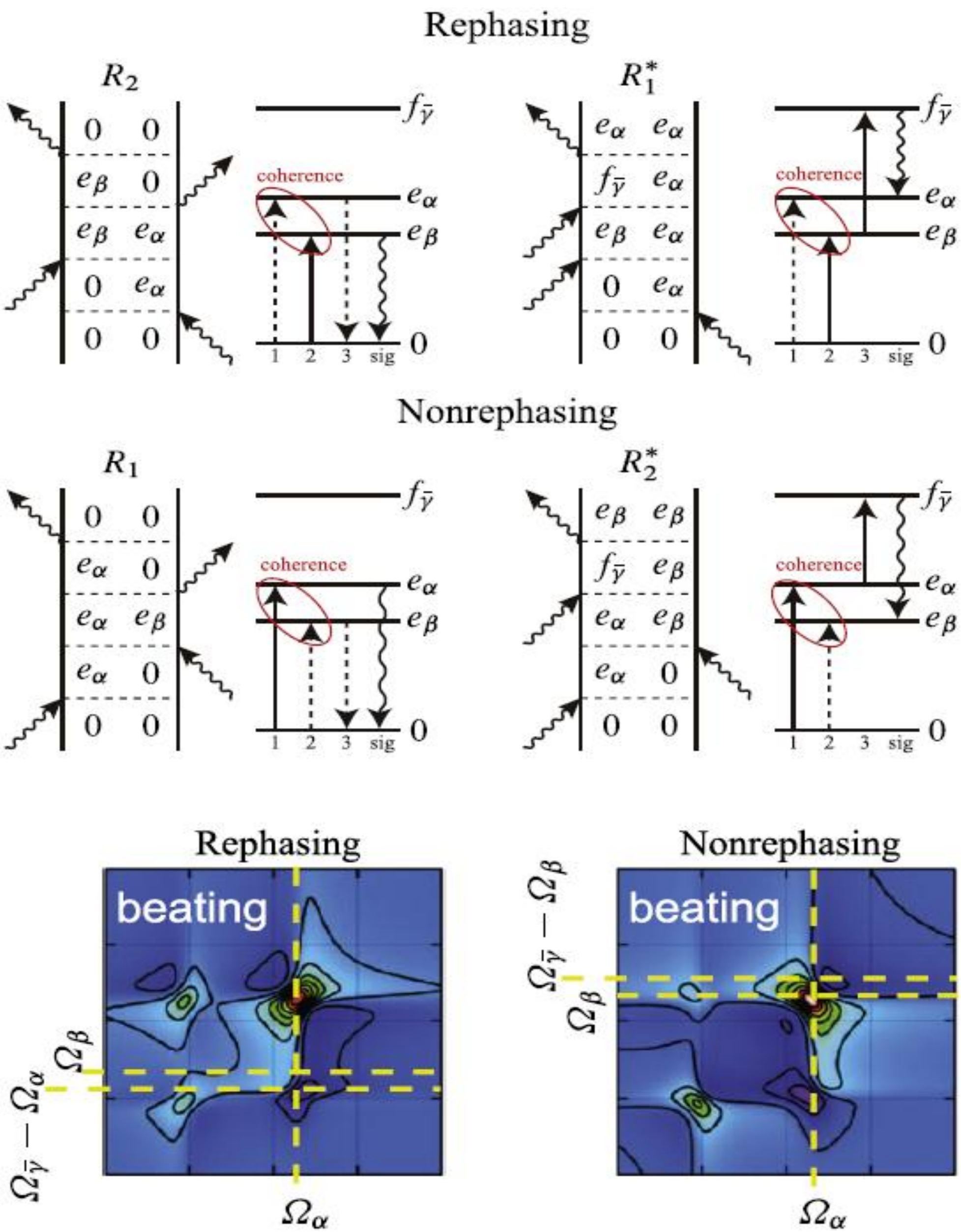
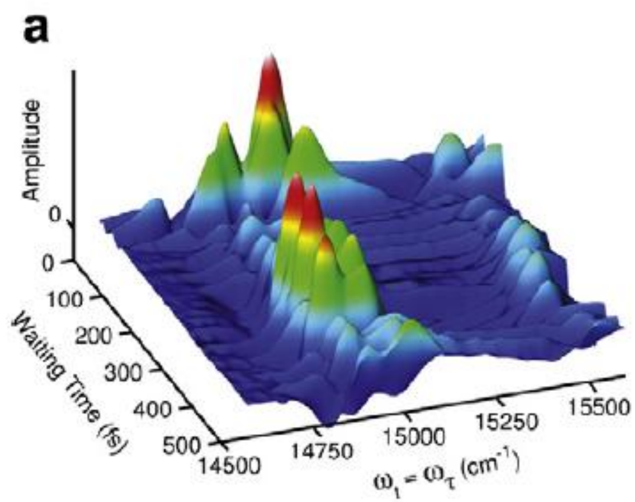


Fig. 1. The evolution of the 2D electronic spectrum of *P. phaeum* FMO is shown. In the conventional 2D spectra (*Left*), the emergence of cross-peaks below the main diagonal is evidenced by the contour lines bowing away from the diagonal by 200 fs. In the cross-peak-specific spectra (*Right*), the emergence of the negative features below the main diagonal corresponds to the cross-peaks largely obscured in the conventional 2D spectra.


Rephasing
R_2
R_1^*
coherence
Nonrephasing
R_1
R_2^*
coherence
1 2 3 sig
Rephasing
Nonrephasing
beating
beating
Ω_β
$\Omega_{\bar{\gamma}} - \Omega_\alpha$
Ω_α
$\Omega_{\bar{\gamma}} - \Omega_\beta$
Ω_β
Ω_α


a
Amplitude
0
Waiting Time (fs)
0
100
200
300
400
500
14500
14750
15000
15250
15500
$\omega_1 = \omega_\tau$ (cm^{-1})