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Beer-Sheva, Israel




Interplay Between Dephasing and Geometry:

Directed Heat Flow in Exciton Transfer Complexes

ICTS International Centre for Theoretical Sciences
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Non-Equilibrium Statistical Physics

26 Oct, 2015 - 20 Nov, 2015

Fondation Adelis

Israel Science Foundation

Feel the Energy

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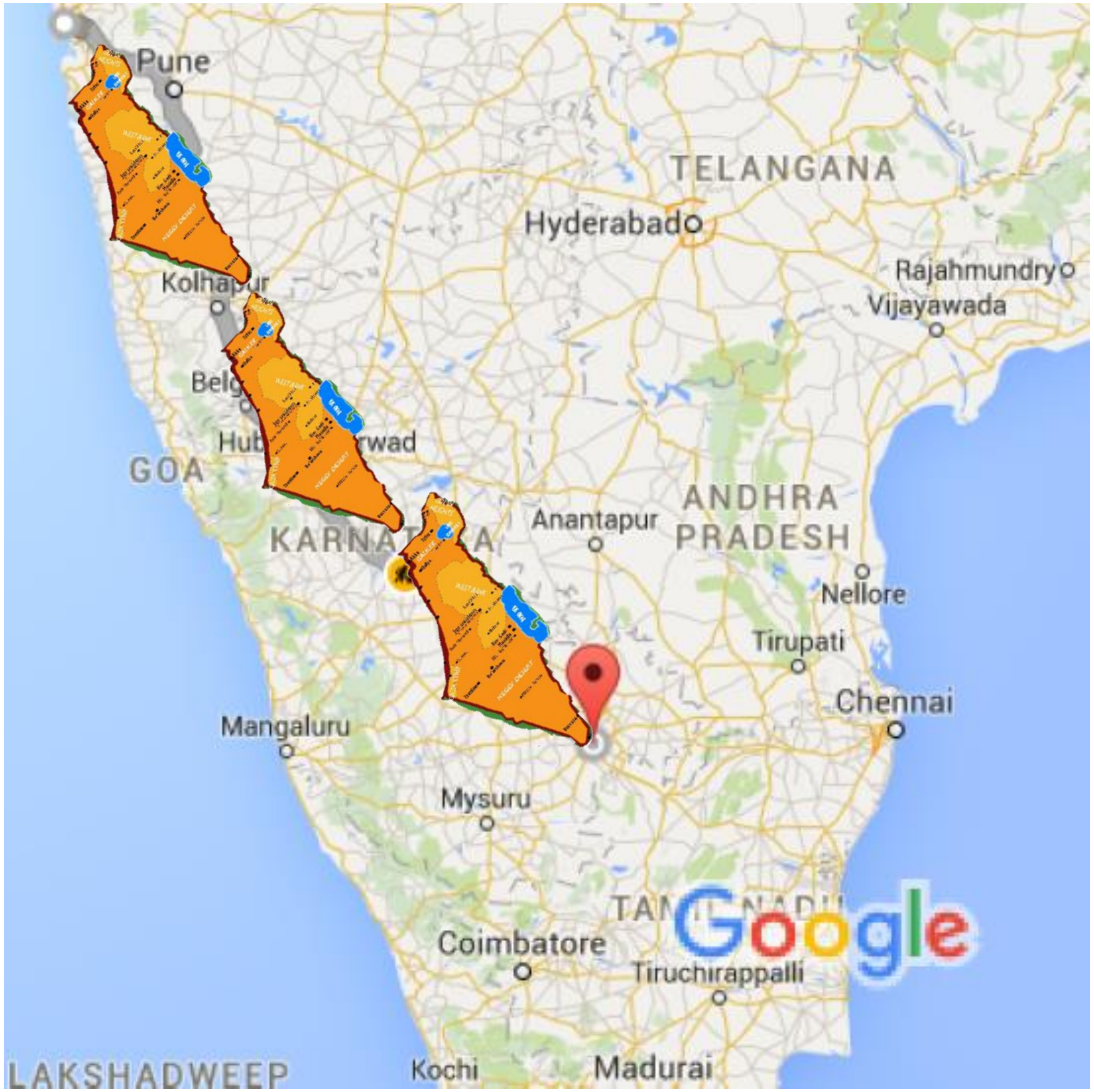
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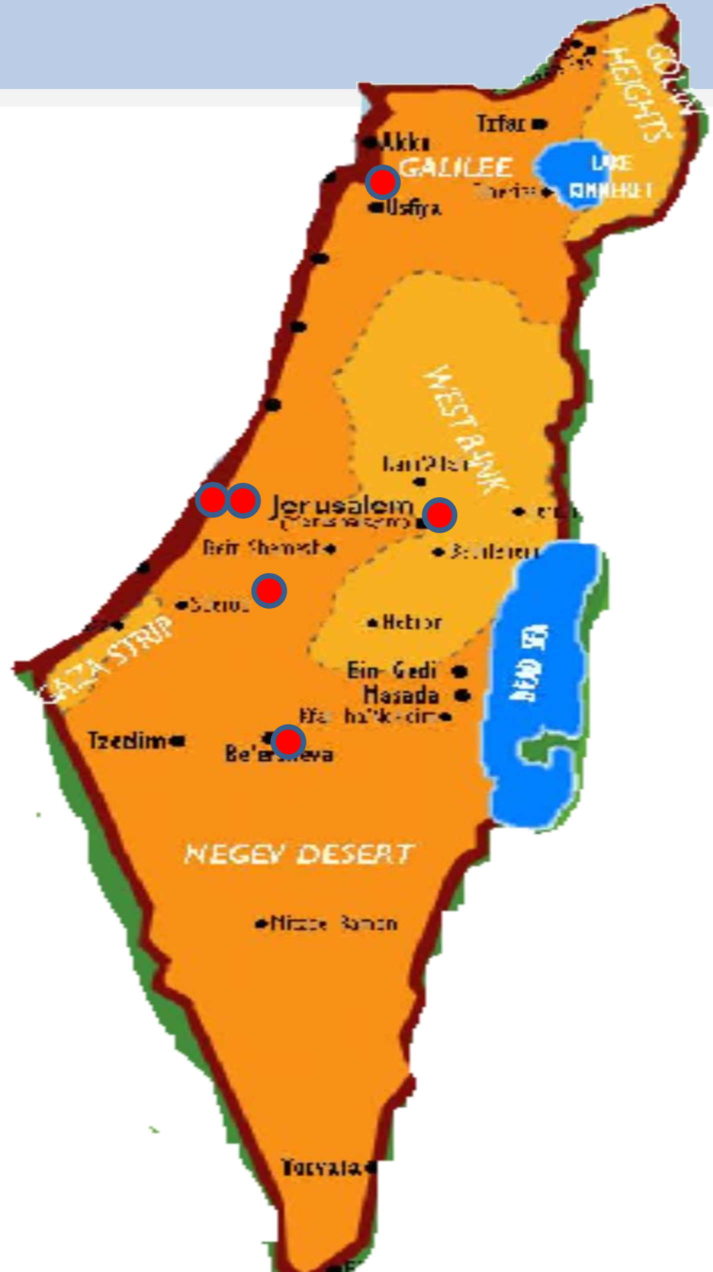
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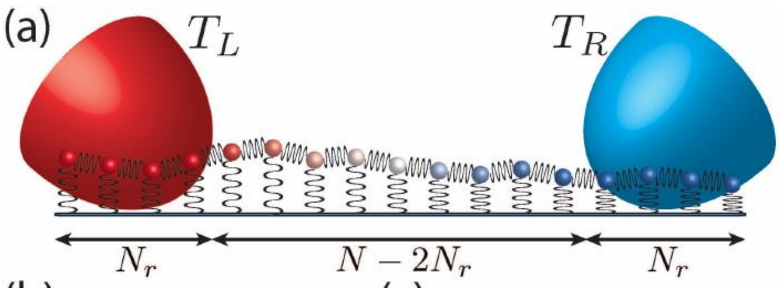
NEGEV DESERT
Yotvata

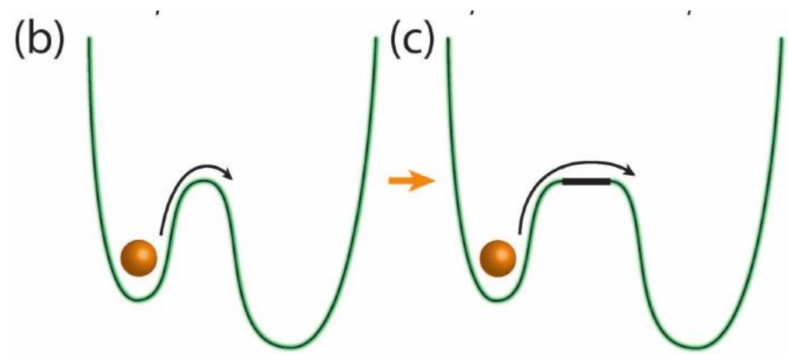
Ask me about thermal transport…

Crossover behavior of the thermal conductance and Kramers' transition rate theory

Kirill A. Velizhanin,[1,*] Subin Sahu,[2,3,4] Chih-Chun Chien,[5] Yonatan Dubi,[6] and Michael Zwolak[2,4,†]

(NPG Scientific Reports, *in press*)



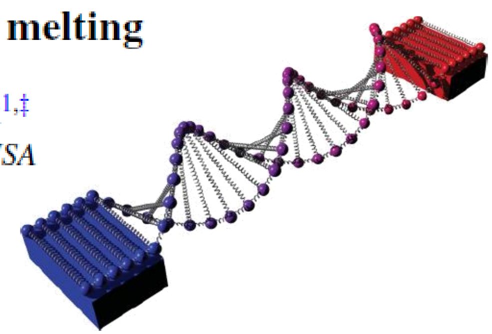


RAPID COMMUNICATIONS

PHYSICAL REVIEW E 83, 050906(R) (2011)

Driving denaturation: Nanoscale thermal transport as a probe of DNA melting

Kirill A. Velizhanin,[1,2,*] Chih-Chun Chien,[1] Yonatan Dubi,[1,†] and Michael Zwolak[1,‡]
[1]*Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*
[2]*CNLS, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*
(Received 15 December 2010; published 19 May 2011)



Outline

Part I:

- Introduction – Quantum Biology?
- Motivation – optical experiments on photosynthetic complexes
- Quick review of current theory

Part II:

- Thinking about *Power*
- Interplay between performance, Geometry and Environment

- Summary & Conclusions

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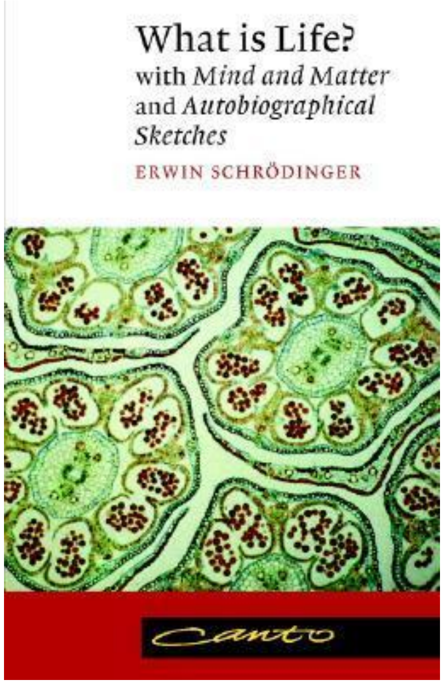
Introduction – Quantum Biology?

Quantum Biology:

the search for “non-trivial” quantum effects in biological systems



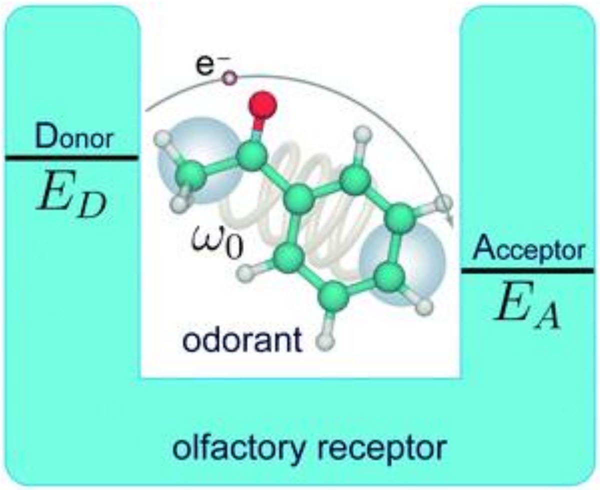
Introduction – Quantum Biology?

Quantum Biology:

the search for “non-trivial” quantum effects in biological systems

Candidates:

- Olfaction (how do we sense molecules by smell?)



Introduction – Quantum Biology?

Quantum Biology:

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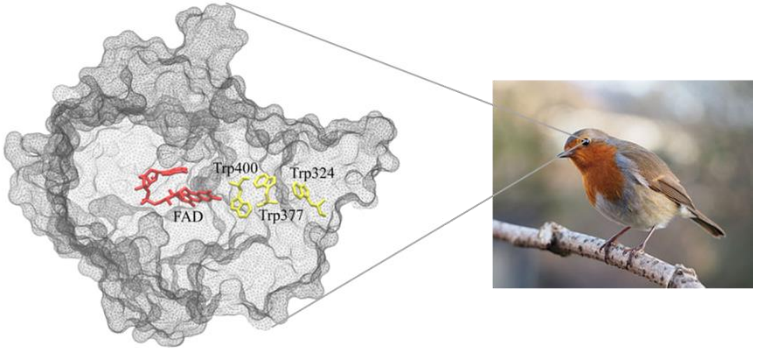
- Olfaction (how do we sense molecules by smell?)
- Avian navigation (how does a Robin find its way from Norway to Egypt?)



Introduction – Quantum Biology?

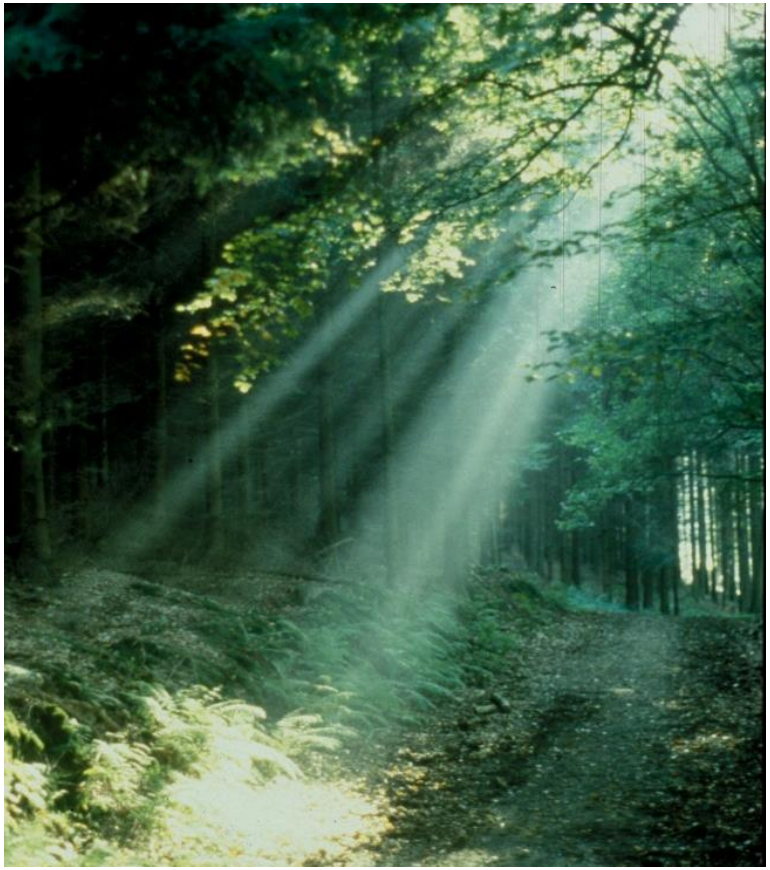
Quantum Biology:

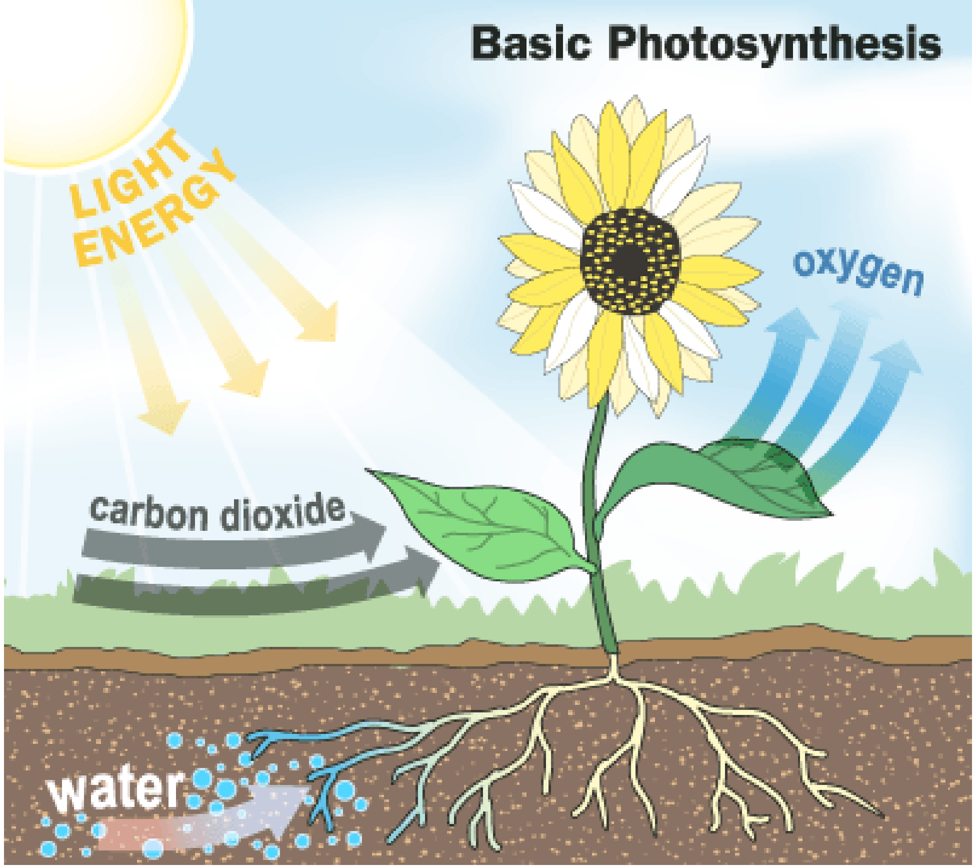
the search for “non-trivial” quantum effects in biological systems

Candidates:

- Olfaction (how do we sense molecules by smell?)
- Avian navigation (how does a Robin find its way from Norway to Egypt?)
- **Photosynthesis**

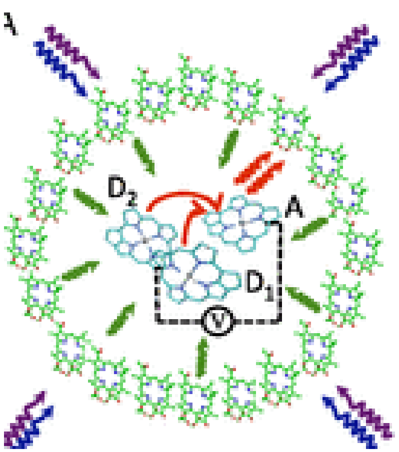
Intro to Photosynthesis





Intro to Photosynthesis

- PS cells – like solar cells – can be viewed as *heat engines*
- They *always* work very far from equilibrium



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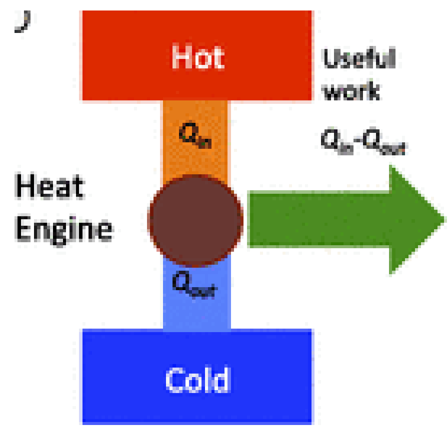
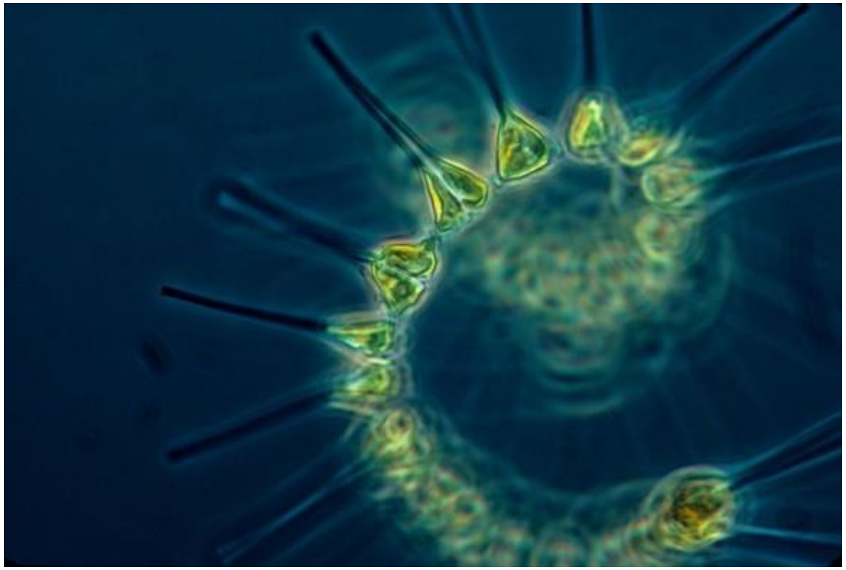


Dorfman, Voronin, Mukamel & Scully PNAS **110**, 2746(2012)

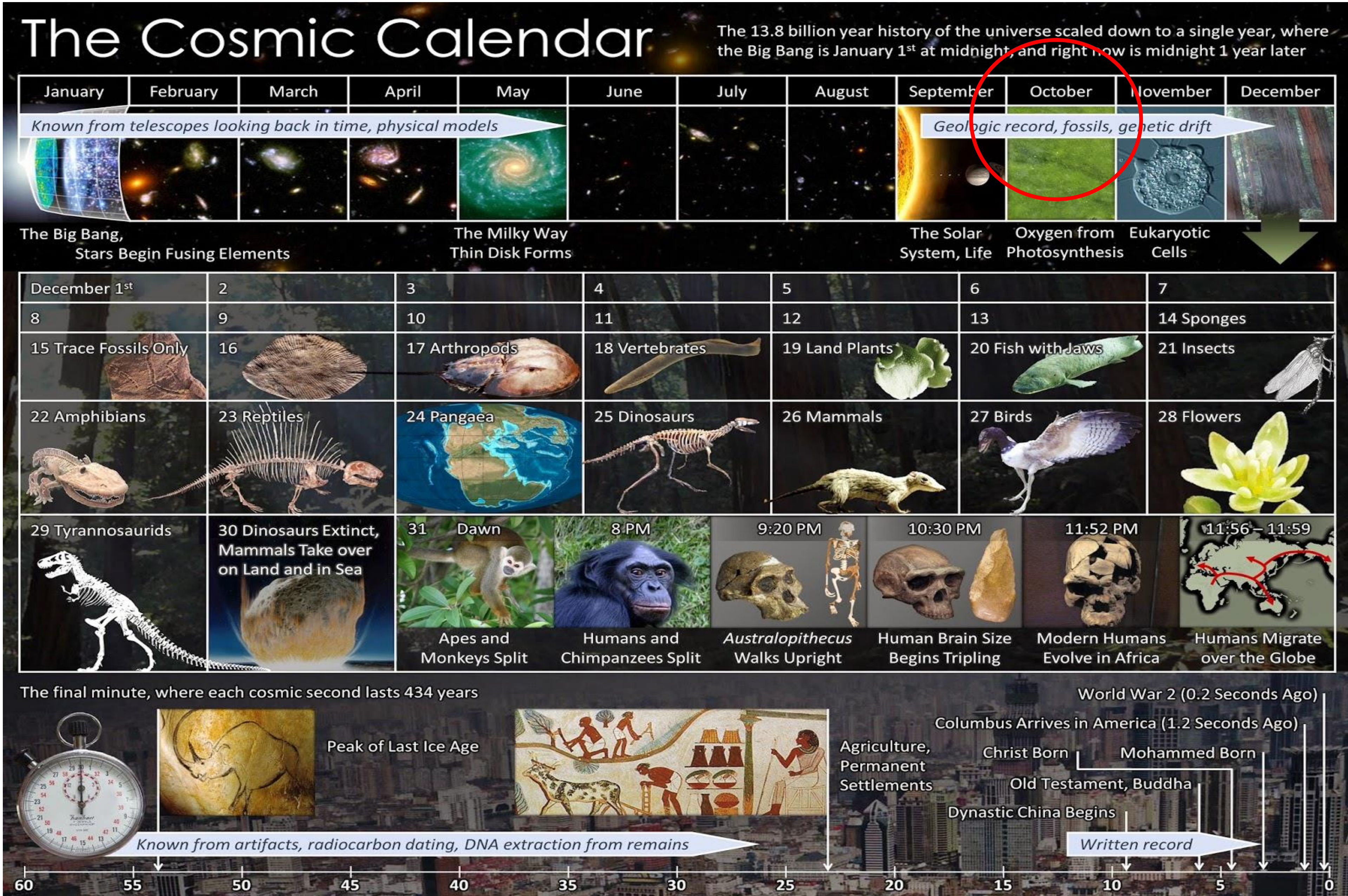
See also Einax, Dierl & Nitzan, J. Phys. Chem. C **115**, 21396–21401 (2011);
Ajisaka, Zunkovitz & Dubi, Sci. Rep. **5**, 8312 (2015).

Intro to Photosynthesis



Phytoplankton – 50-85% of the oxygen on planet earth

Intro to Photosynthesis



Intro to Photosynthesis

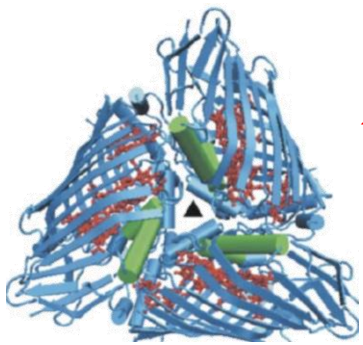
The “fruit-fly” of

photosynthesis –

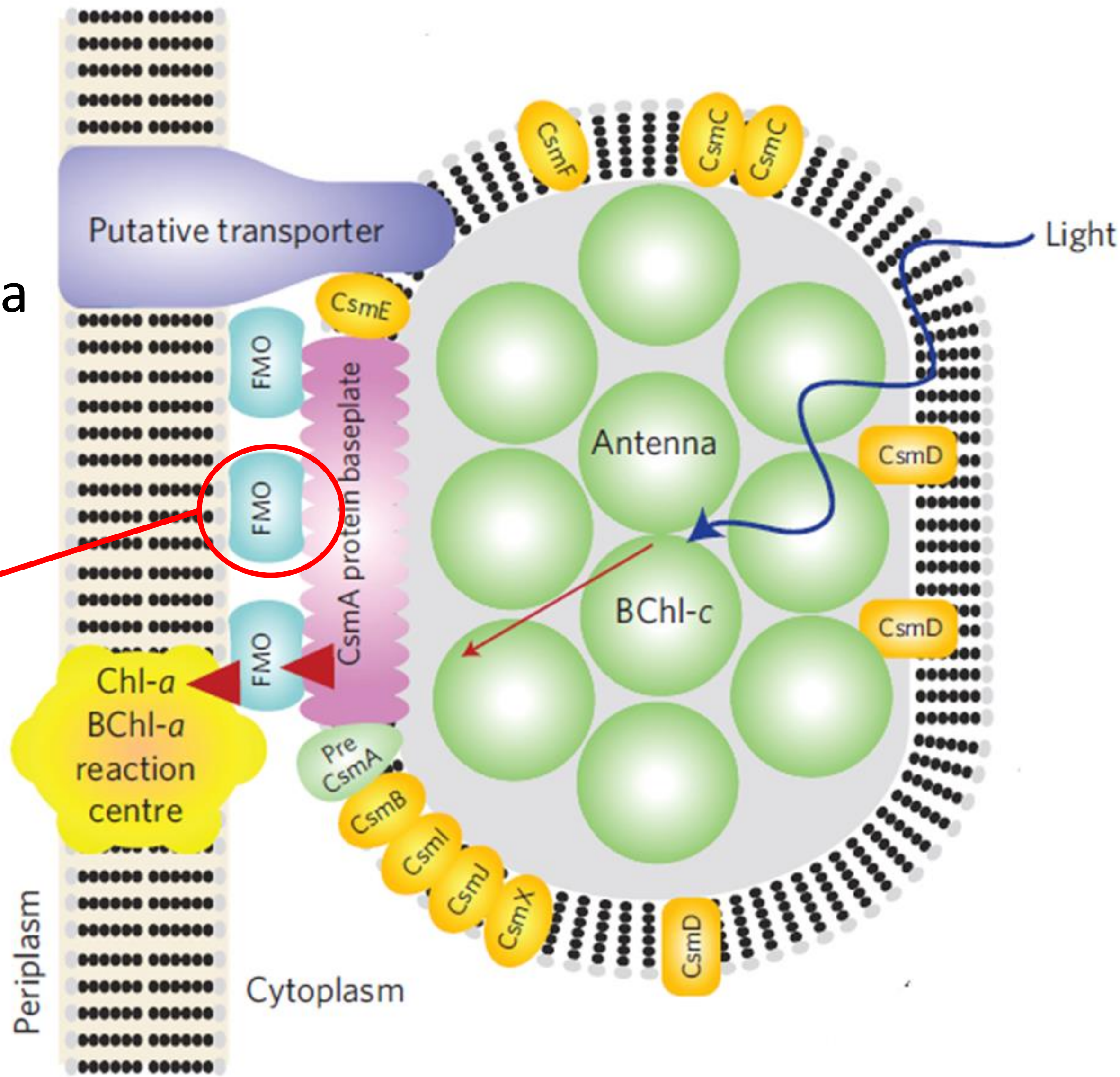
the Green Sulfur Bacteria

Intro to Photosynthesis

The "fruit-fly" of photosynthesis – the Green Sulfur Bacteria

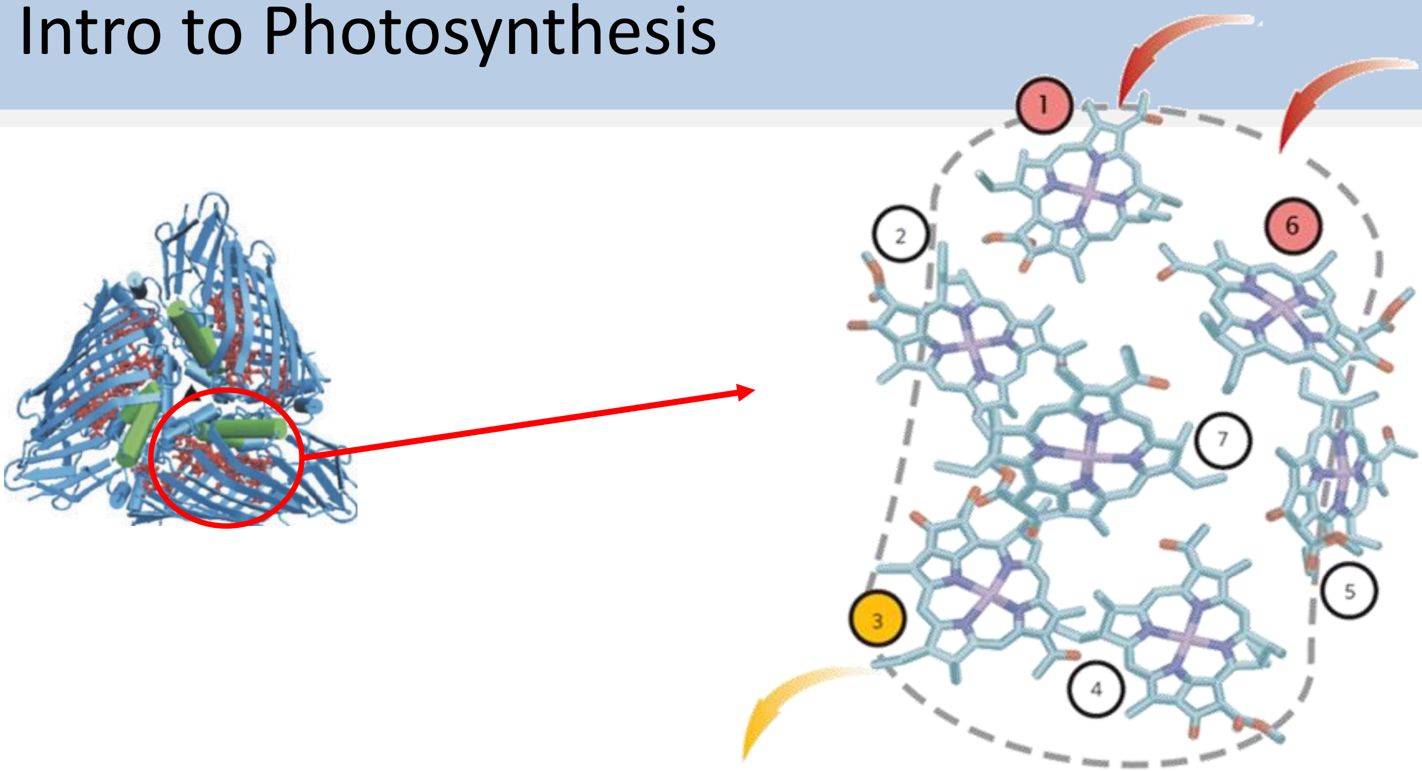


Muh *et al.*, PNAS **104**, 16862 (2007)



James Allen *et al.*, Photosynth. Res., **75**, 49 (2003)

Intro to Photosynthesis



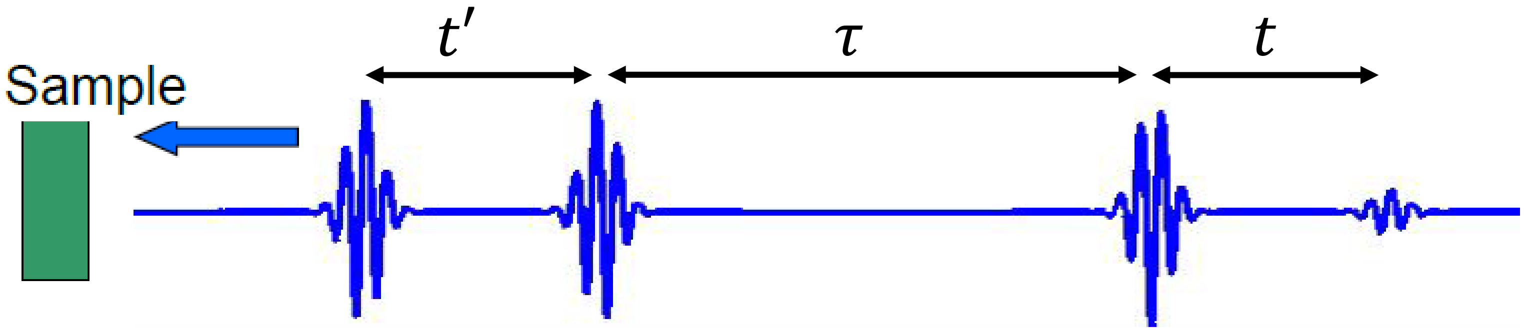
The system is well-characterized:

$$\mathcal{H} = \sum_{n=1}^{7\,(8)} E_n |n\rangle\langle n| + \sum_{n,m} t_{nm} |n\rangle\langle m|,$$

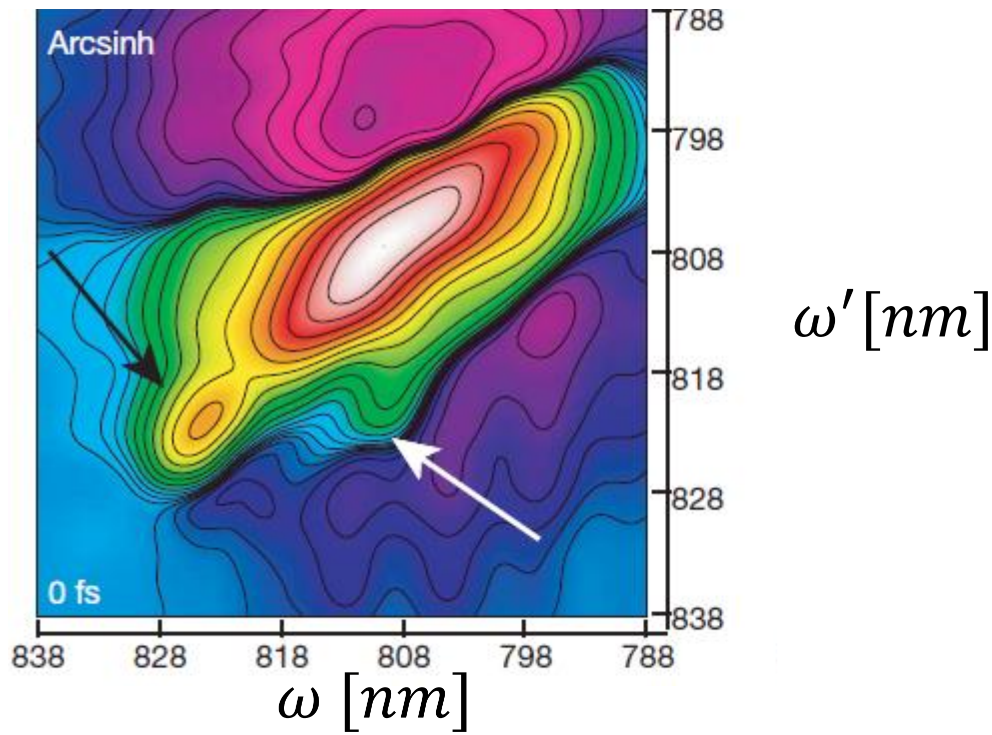
E_n , t_{nm} extracted from pump-probe experiments

Experiments revile Quantum Coherence

2D-Electronic Spectroscopy:

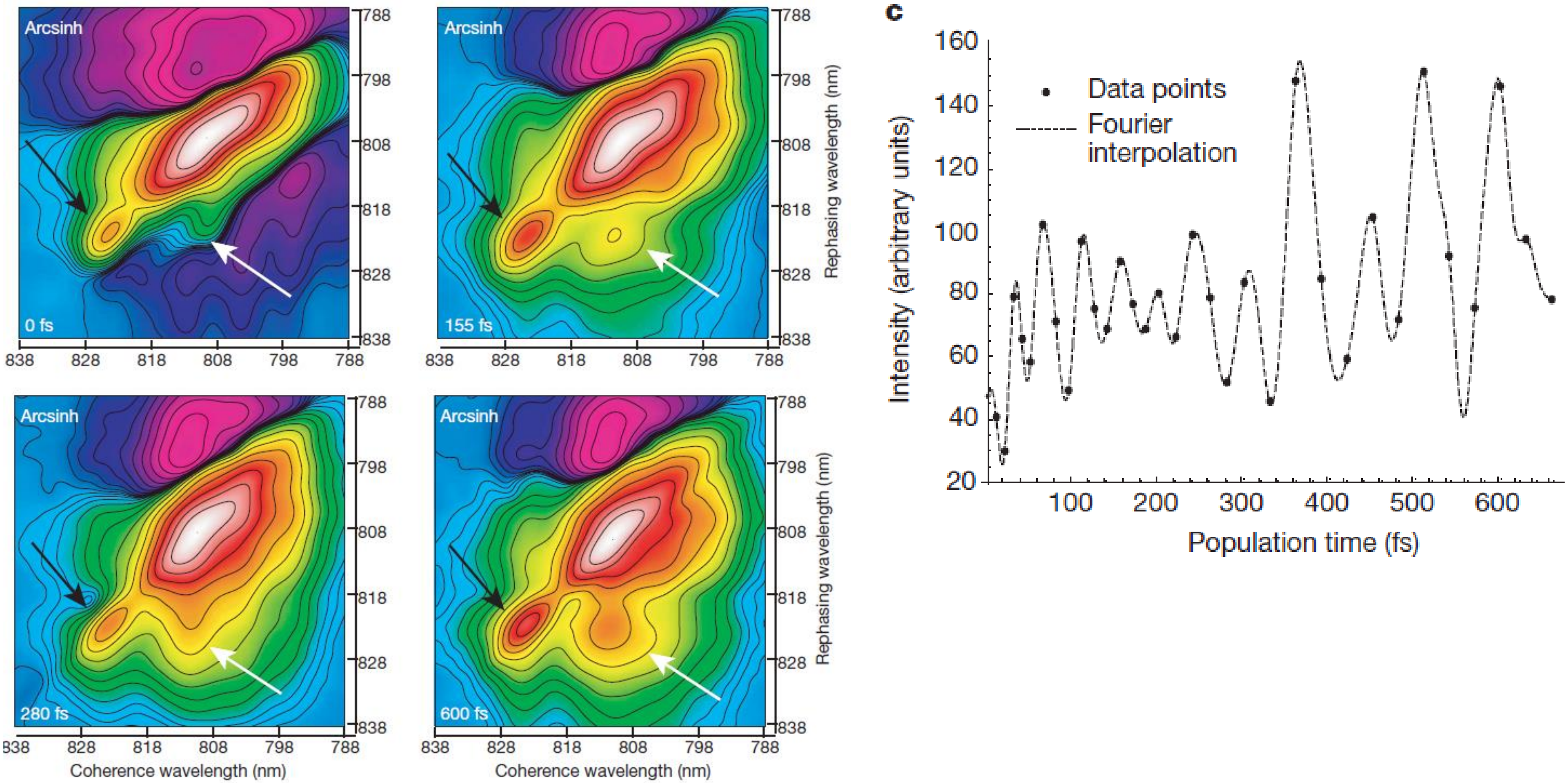


Fourier transform in *t, t'*



Engel *et al.*, Nature **446**, 5678 (2007)

Experiments revile Quantum Coherence



Engel *et al.*, Nature **446**, 5678 (2007)

Experiments revile Quantum Coherence

Quantum Coherence in Exciton Transfer Complexes (ETC):

1. Is it real?

2. How is coherence maintained in a “wet and floppy environment”?

3. Dows nature *use* this coherence for ETC optimization?

(Optimization: Stability, Photoprotection, Efficiency)*

Theory of Quantum coherence in ETC – short intro

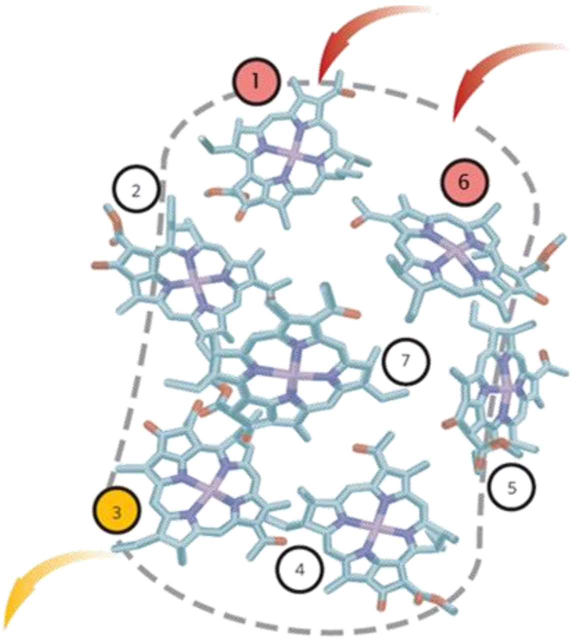
The general structure of theory in ETC analysis:

(i) Hamiltonian: $\mathcal{H}_{FMO} = \sum_{n=1}^{7\,(8)} E_n |n\rangle\langle n| + \sum_{n,m} t_{nm} |n\rangle\langle m|$

(ii) Environment: $\mathcal{H}_{env} = \sum_q \omega_q a_q^+ a_q$

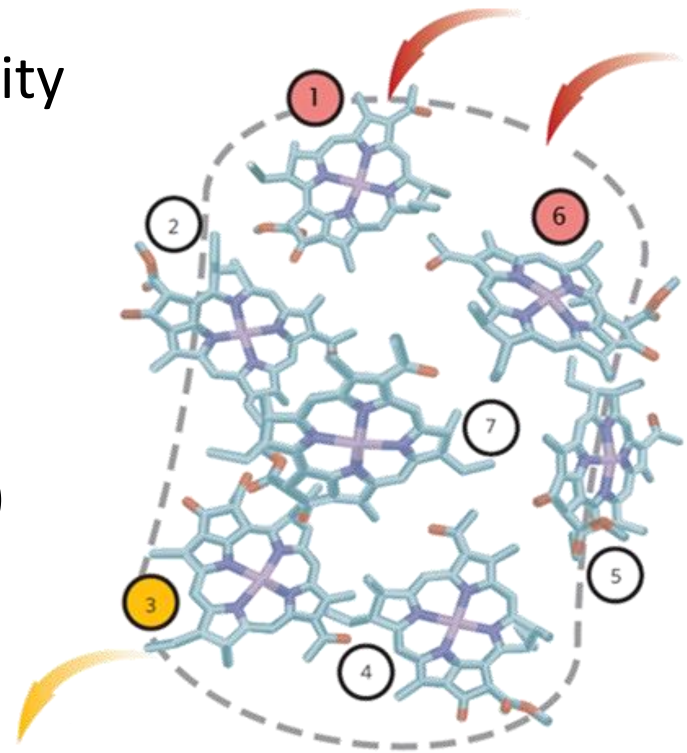
(iii) Coupling: $\mathcal{H}_c = \sum_{n,q} \lambda_{n,q} \left(a_q^+ + a_q\right) e_n^+ e_n$

(iv) Spectral density $J(\omega) = \sum_q \lambda_q^2 \delta\left(\omega - \omega_q\right)$



Theory of Quantum coherence in ETC – short intro

What to calculate? *Vast* majority: local density



1. Excite exciton at site 1 or 6 or both
2. Evaluate dynamics

   (via density matrix, $\dot{\rho} = -i[\mathcal{H}, \rho] + \mathcal{L}\rho$)

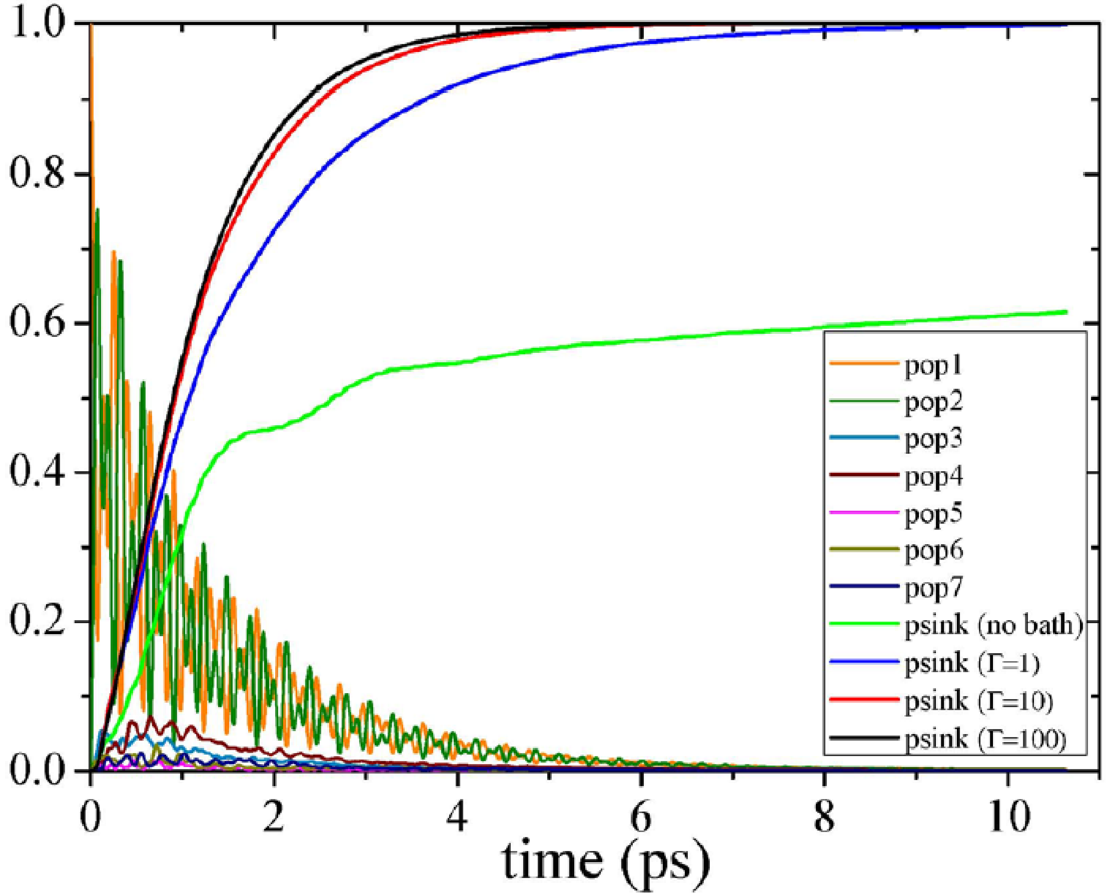
3. Calculate exciton density at cite 3

Efficiency is *defined* as :

$$\eta_3 = \gamma_3 \int_0^\infty \rho_{33}(t) dt$$

Theory of Quantum coherence in ETC – short intro

Typically looks something like this:



Chin, Datta, Caruso, Huelga & Plenio, New. J. Phys. **12**, 065002 (2010)

Theory of Quantum coherence in ETC – short intro

Efficiency is enhanced in the presence of dephasing

Plenio, M. B. and Huelga, S. F. *New Journal of Physics* **10**, 113019 (2008);
Rebentrost, P., Mohseni, M., Kassal, I., Lloyd, S.; Aspuru-Guzik, A., *New Journal of Physics* **11,** 033003 (2009).

(mechanism still unclear…)

Some Review:

Ishizaki & Fleming, Annu. Rev. Condens. Matter Phys (2012);
Huelga & Plenio, Nature Phys. (2014); Fleming, Huelga & Plenio, New J. Phys. (2011);
Collini, Chem. Soc. Rev. (2013); Scholes & Fleming, Adv. Chem. Phys. (2005);
Pachon & Brumer, PCCP (2012); Scholes, Nat. Phys. (2011);
Scholes & Smyth, J. Chem. Phys. (2014).

What can we add? (*aims*)

- How is the (standard) efficiency behaves?
- What is its relation to η_3 ?
- What is the *origin* for dephasing-enhanced efficiency?

- The ETC is an *energy-conversion* device
- Excitons (as opposed to electrons) do not carry charge:

  Exciton current is not simply related to energy current!

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A *Heat-Current* approach to exciton transport

This approach:

- Takes into account the source (antenna) and sink (reaction center
- Implies incoherent energy input
- Directly calculate Power output

A *Heat-Current* approach to exciton transport

Starting point: the full (many-body) FMO Hamiltonian

$$\mathcal{H}_{FMO} = \sum_{n=1}^{7} E_n\, c_n^{+} c_n + \sum_{n,m} t_{nm}\, c_n^{+} c_m$$

Then use the Lindblad Equation

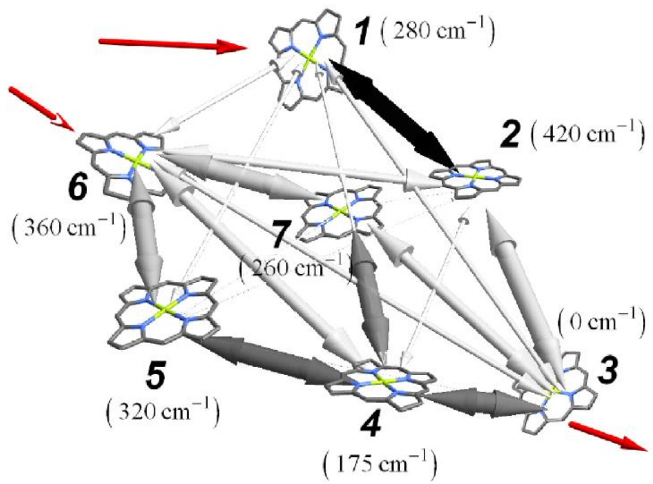
$$\dot{\rho}(t) = -\frac{i}{\hbar}[\mathcal{H}, \rho(t)] + \hat{\mathcal{L}}[\rho(t)],$$

$$\hat{\mathcal{L}}[\rho(t)] = \sum_i \left(-\frac{1}{2}\{V_i^{\dagger} V_i, \rho\} + V_i \rho V_i^{\dagger} \right)$$

Pros:

- Proper quantum equation
- Simple physical interpretation

Cons: Phenomenological, no memory



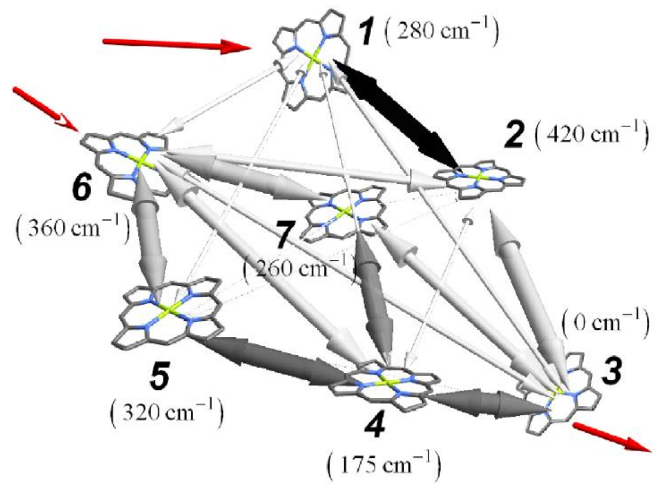
A *Heat-Current* approach to exciton transport

The V-operators encode different physical processes:

$$V_{deph} = \sqrt{\gamma_{deph}} c_n^+ c_n \,, \quad \gamma_{deph} = \tau_{deph}^{-1}$$

$$V_{in} = \sqrt{\gamma_{in}} c_1^+, \sqrt{\gamma_{in}} c_6^+,$$

$$V_{out} = \sqrt{\gamma_{out}} c_3$$



A *Heat-Current* approach to exciton transport

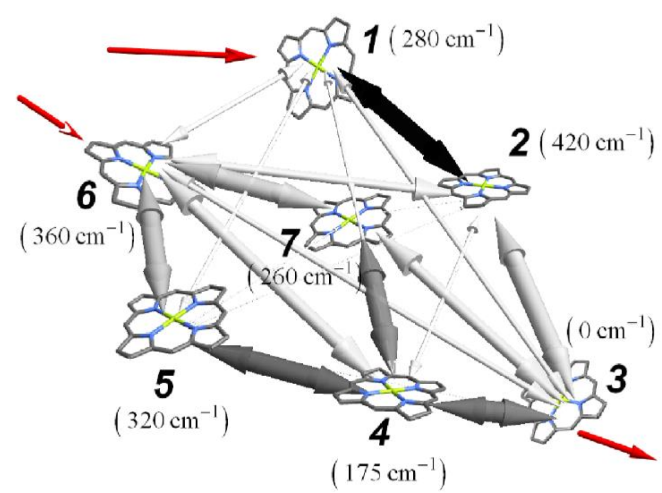
The properties of the system are determined from the *Steady state:*

$$\dot{\rho}_\infty = -\frac{i}{\hbar}[\mathcal{H}, \rho_\infty] + \hat{\mathcal{L}}[\rho_\infty] = 0$$

Heat currents can be calculated as:

$$\dot{Q}_{in} = Tr(-M_{source}\rho_\infty\mathcal{H})$$

$$\dot{Q}_{out} = Tr(-M_{sink}\rho_\infty\mathcal{H})$$



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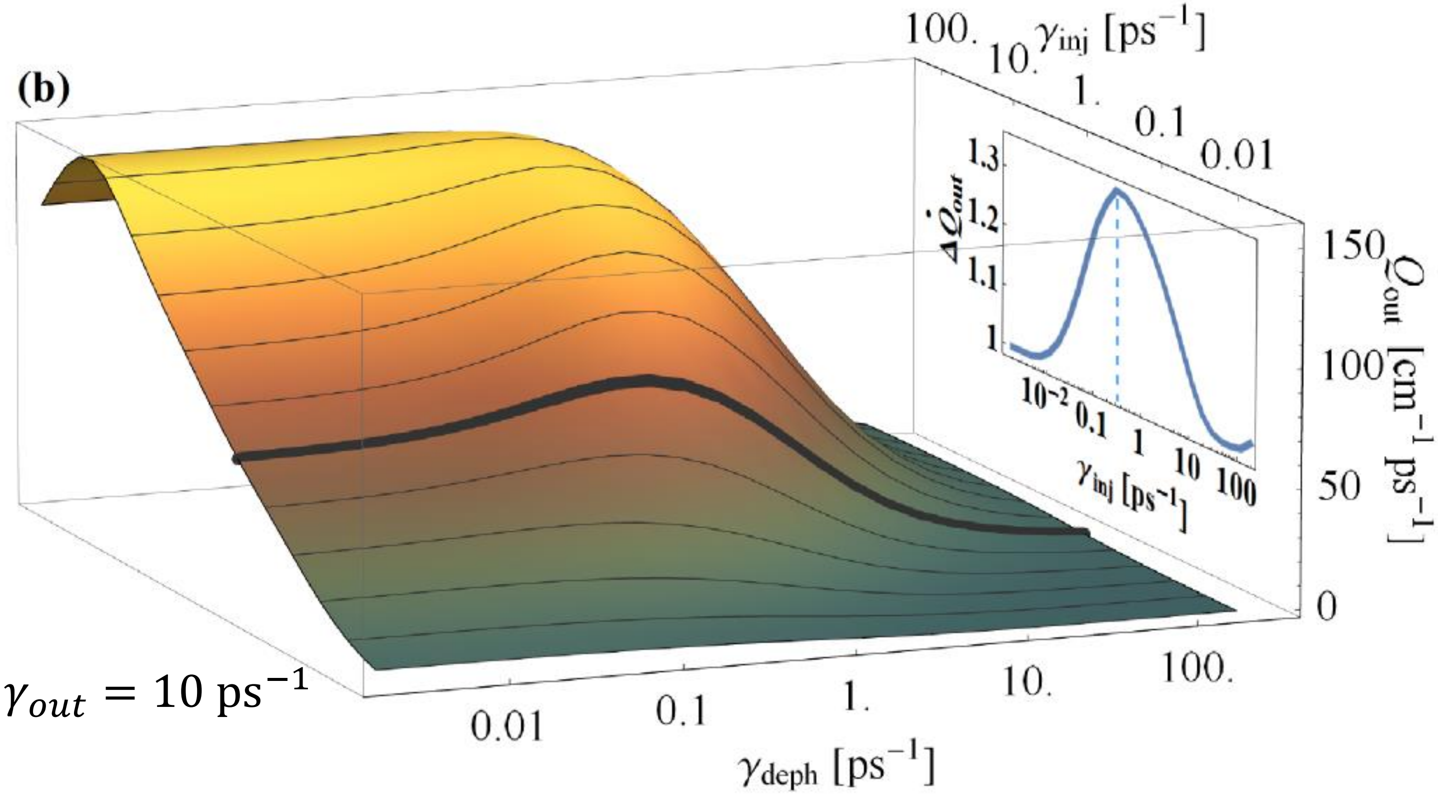
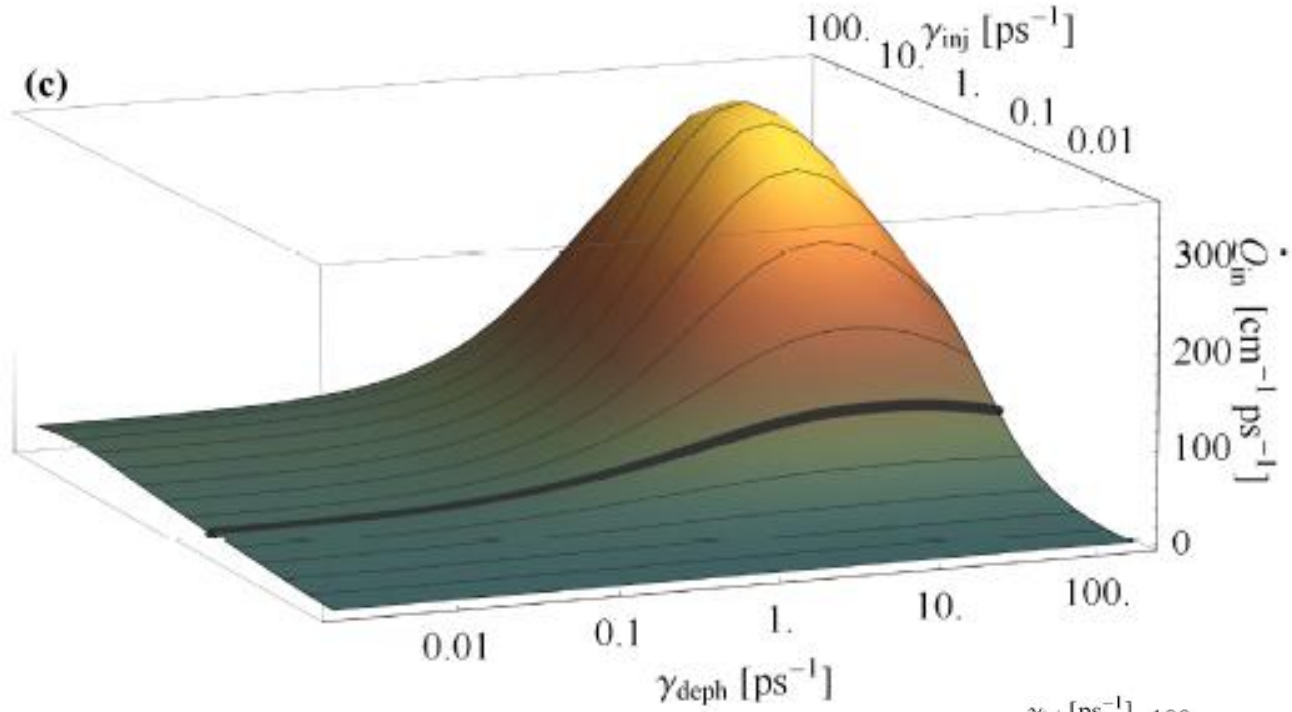
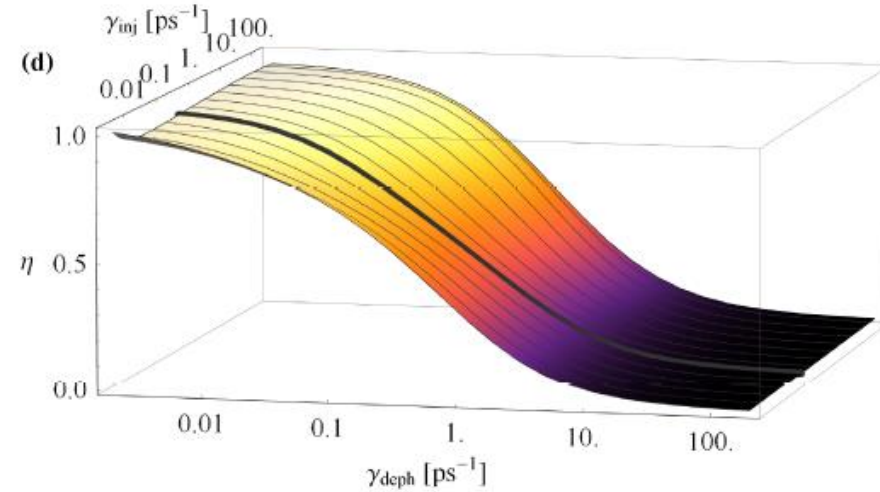


$\gamma_{out} = 10\ \mathrm{ps}^{-1}$

- Dephasing assists power output!
- Optimal rates $\gamma_{inj} \sim \gamma_{deph} \sim 0.5\ \mathrm{ps}^{-1}$ (“Goldilocks” effect)

A *Heat-Current* approach to exciton transport

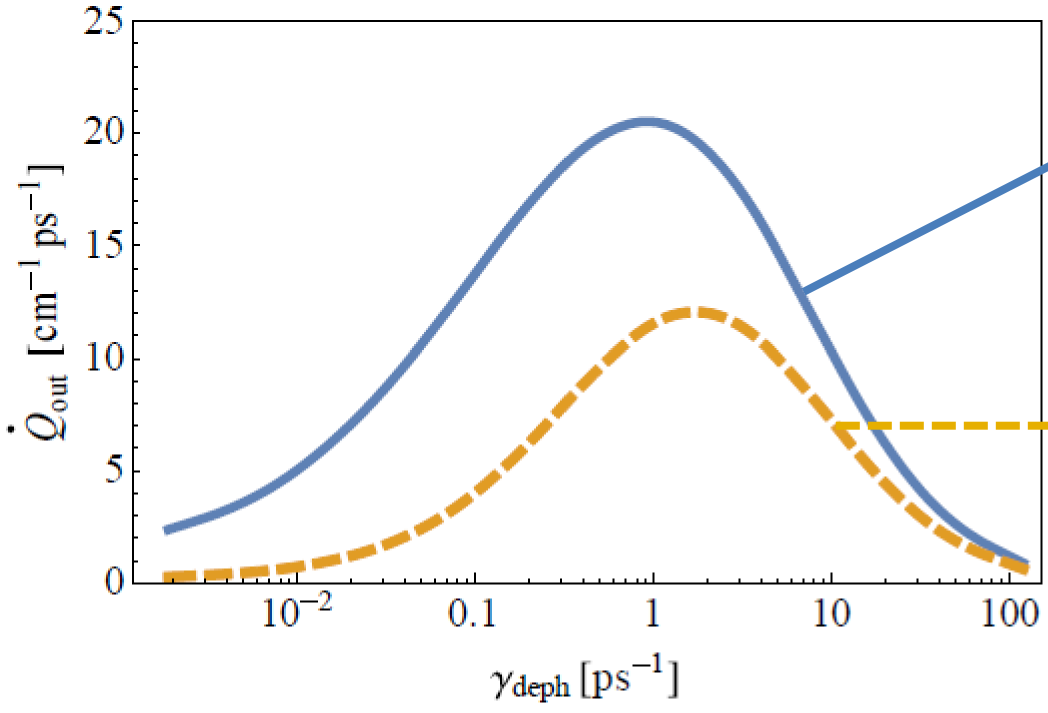


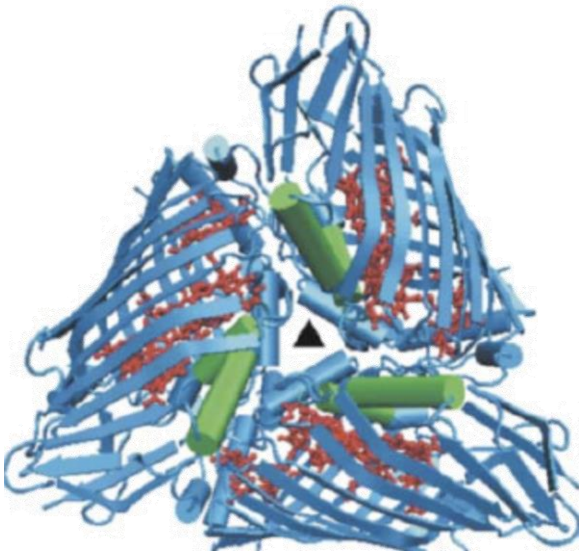


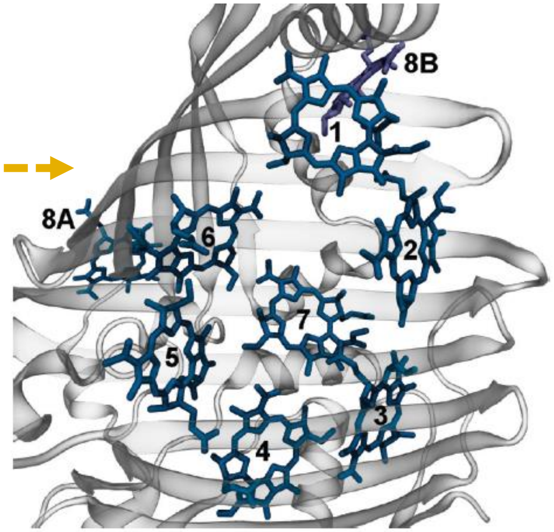
A *Heat-Current* approach to exciton transport

How general is this effect?

It holds for different geometries:

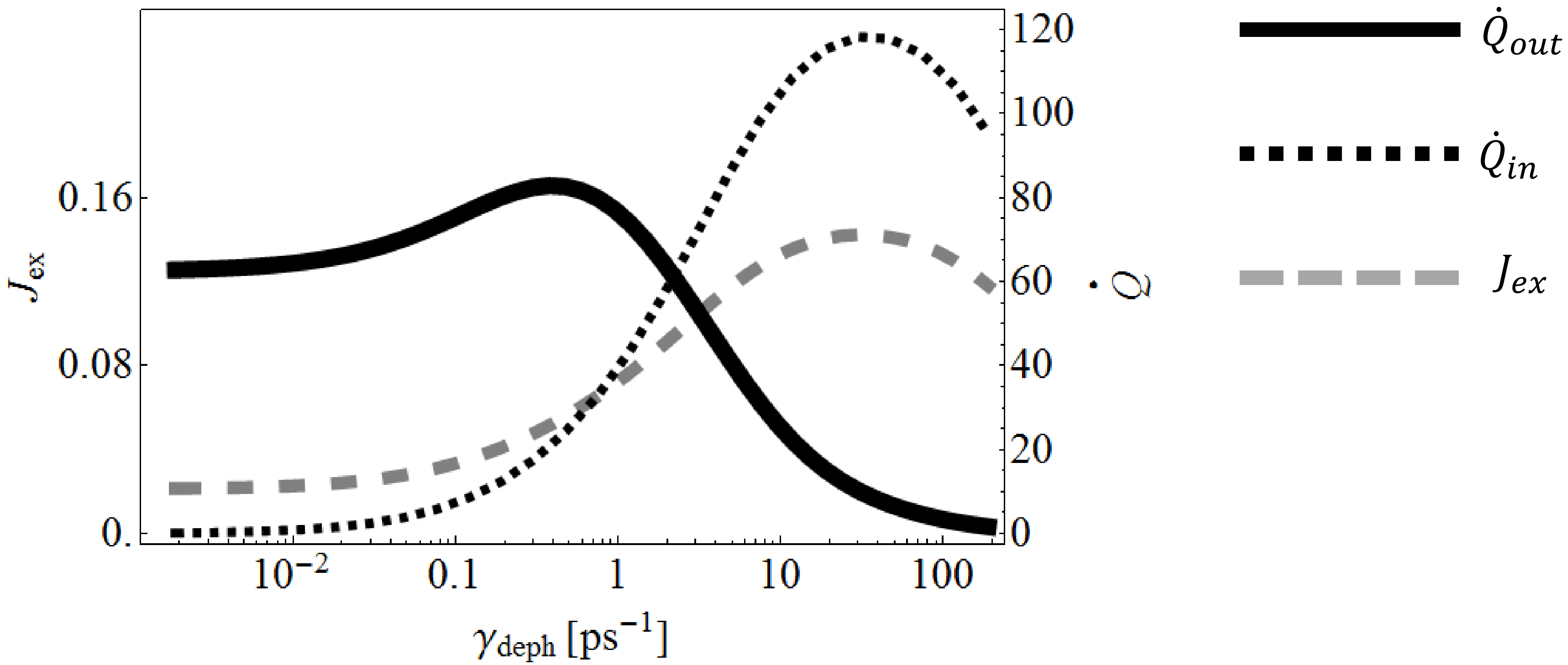






A *Heat-Current* approach to exciton transport

Heat current vs. *exciton current:*



Interplay between Geometry and Environment

Dephasing-induced enhancement of power output:

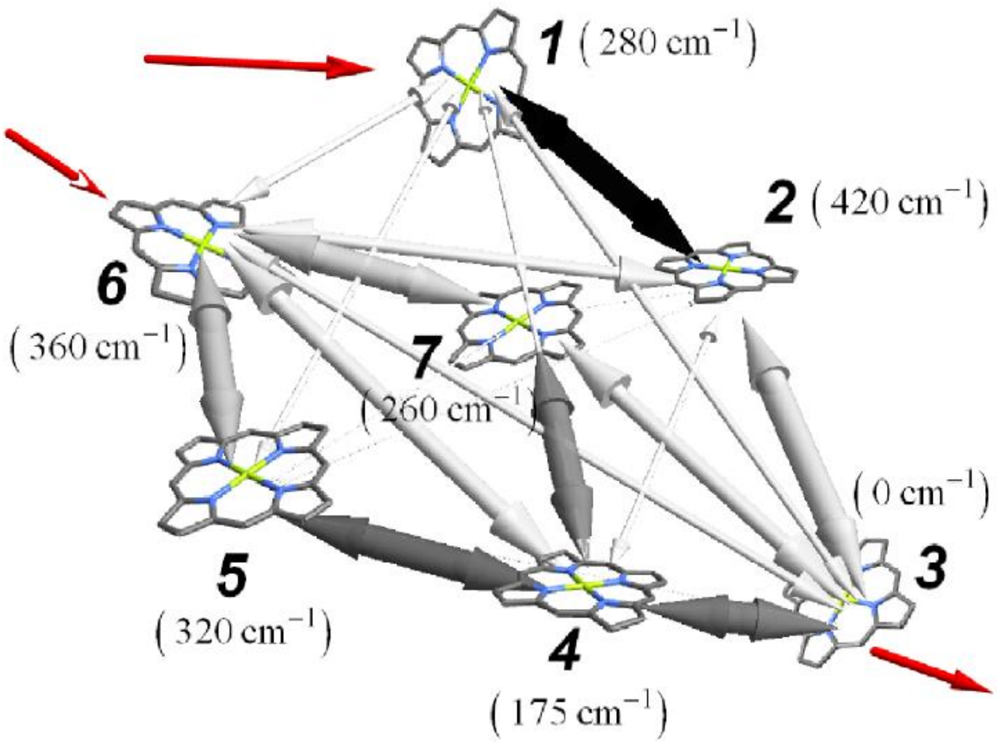
- What is the origin for the excitonic effect?
  - delocalization (noise-induced level alignment)
  - Oscillation damping
  - Momentum rejuvenation (large lattices)

- Does (and how) it involve the Geometry of the network?

Interplay between Geometry and Environment

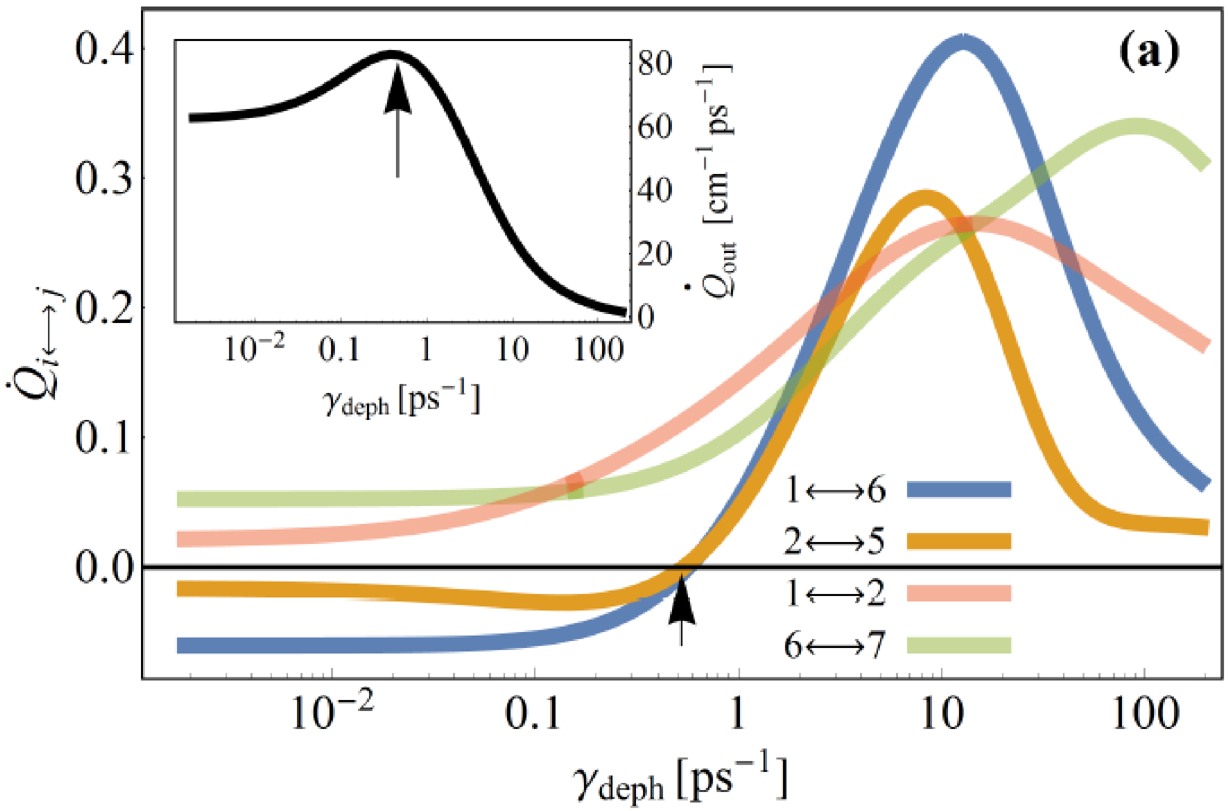
Calculating local heat currents:

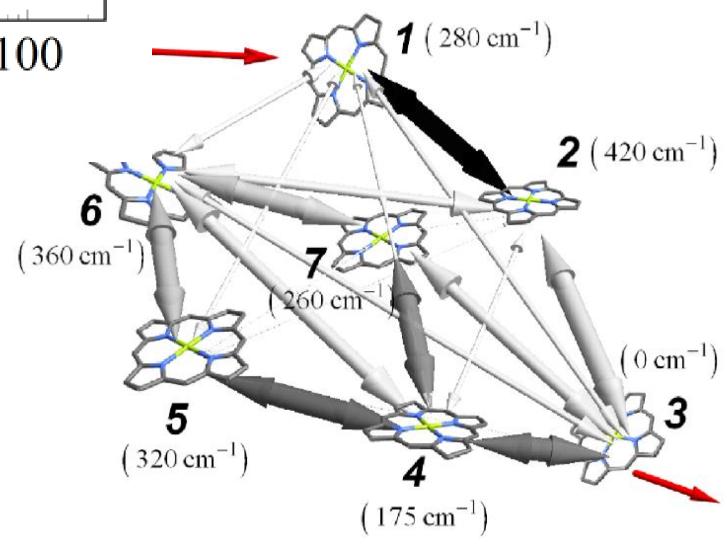
$$\frac{d}{dt}\langle h_i\rangle = -i\,Tr\left([\,h_i,\mathcal{H}]\rho_\infty\right) - Tr\left(\,h_i\widehat{M}\rho_\infty\right) = \sum_j \dot{Q}_{i\leftrightarrow j}$$



Wu & Segal., *J. Phys. A: Math. Theor.* **2009**, 42, 025302

Interplay between Geometry and Environment

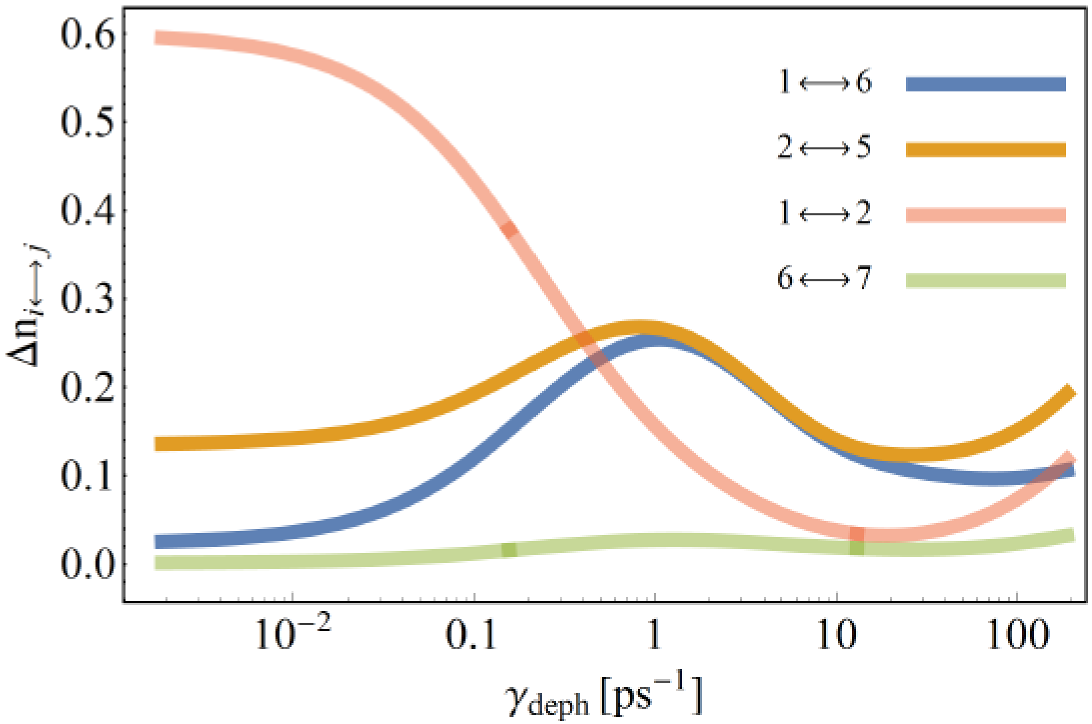




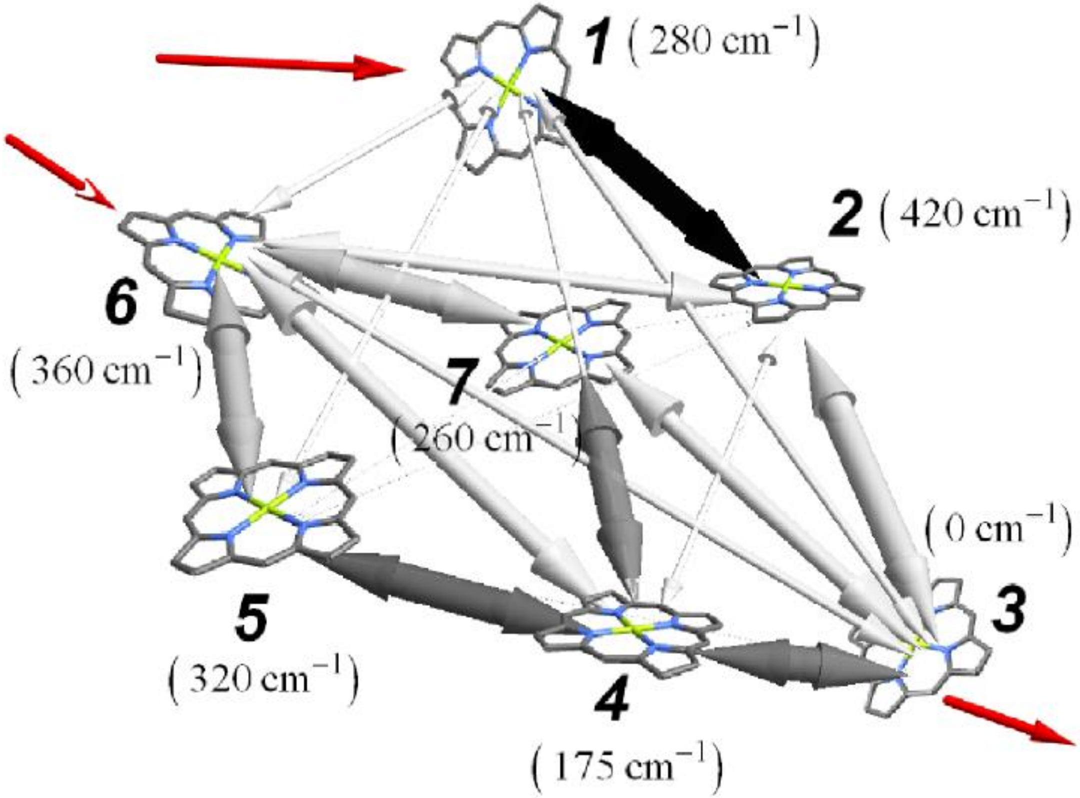
- “inter-branch” heat current vanishes at optimal dephasing!
- …but “intra-branch” does not

Interplay between Geometry and Environment

Immediate suspect: density differences - not the origin

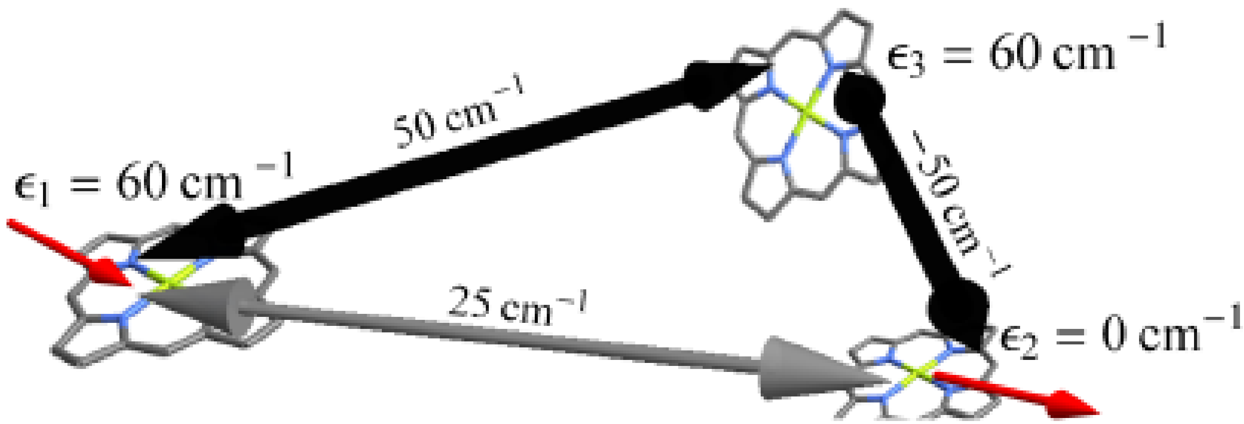


Directed Heat Flow



Directed Heat Flow

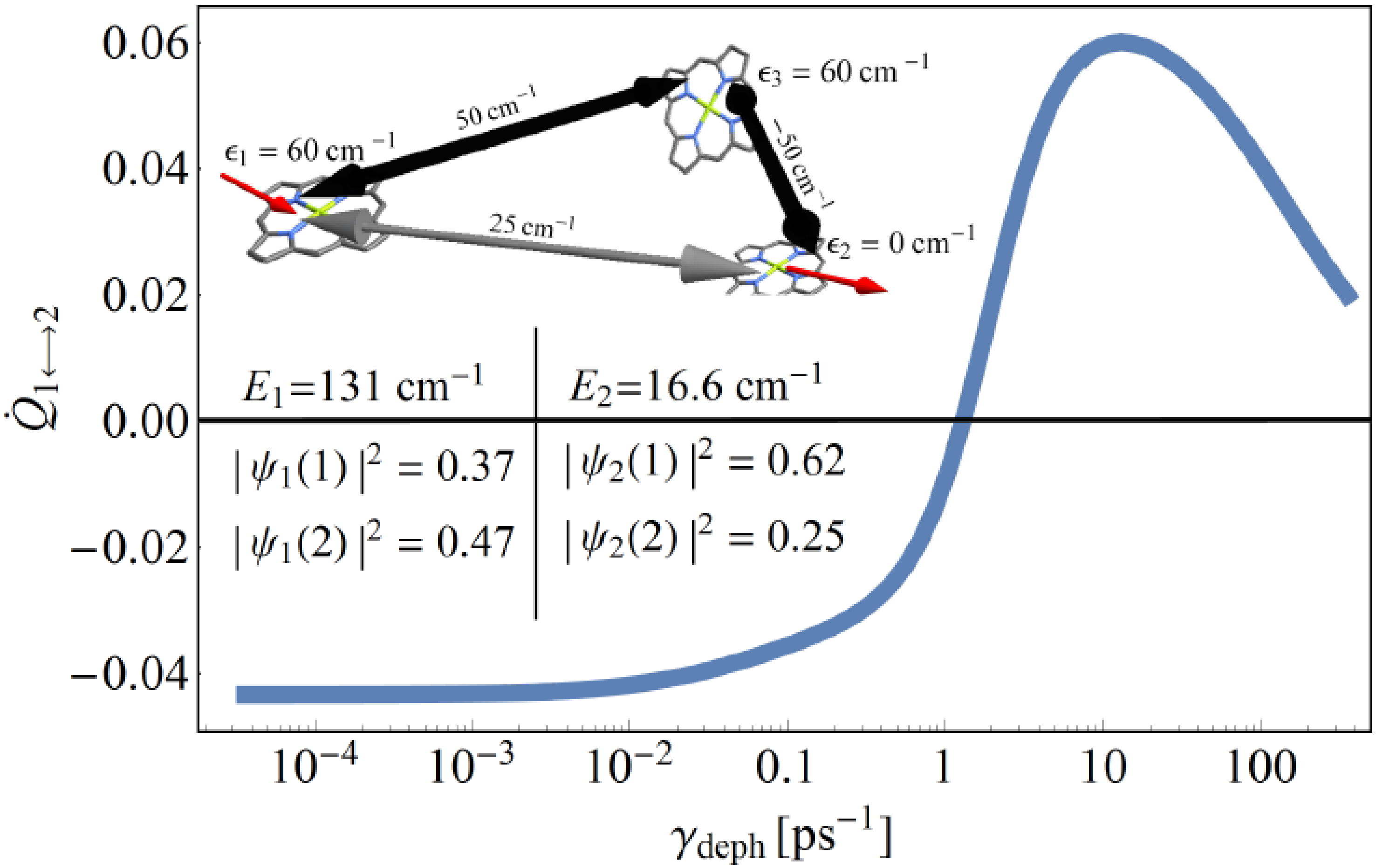
An analytically soluble minimal model:



Vanishing dephasing limit: $\dot{Q}_{1\leftrightarrow 2} \approx -\frac{t_0\gamma(\epsilon_1-\epsilon_2)(\epsilon_1-\epsilon_2+t_0)}{(\epsilon_1-\epsilon_2+t_0)^2+6\,t_0^2}$

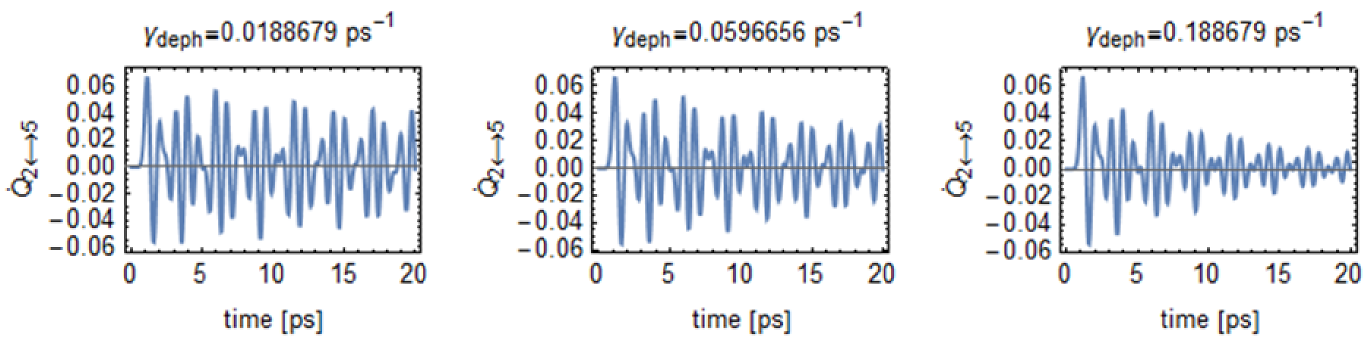
Strong dephasing limit: $\dot{Q}_{1\leftrightarrow 2} \approx \frac{t_0(\epsilon_1-\epsilon_2)}{\gamma_{deph}}$

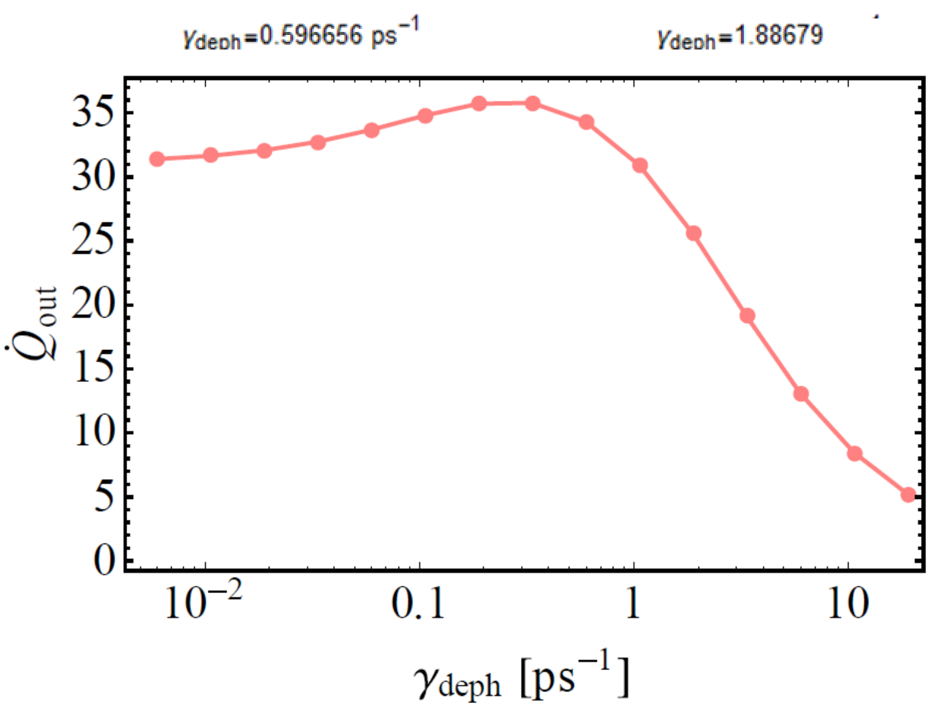
An analytically soluble minimal model:

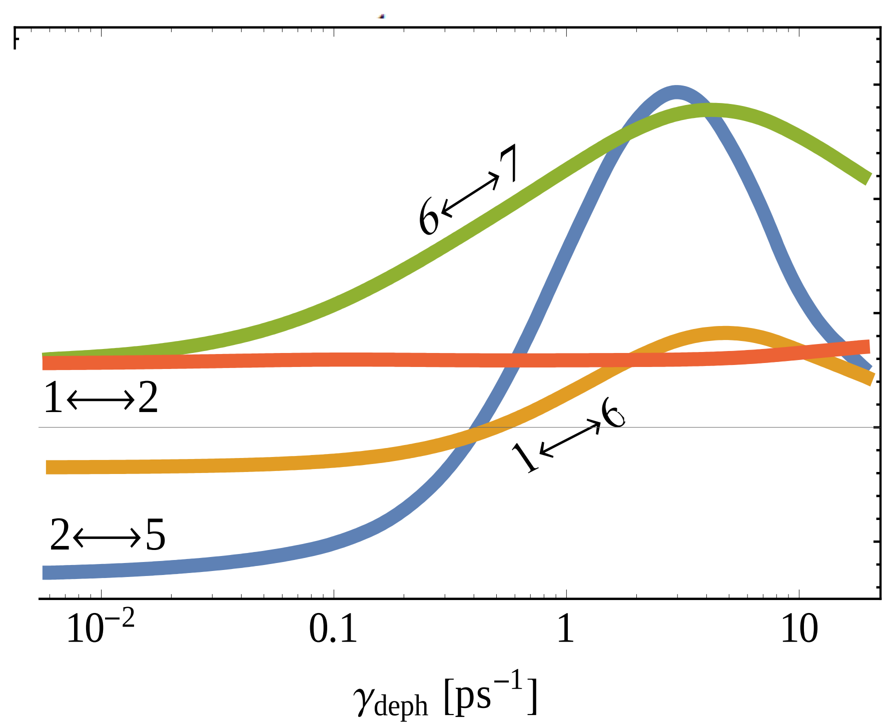


Directed Heat Flow

The mechanism works even for pulse-excitation:



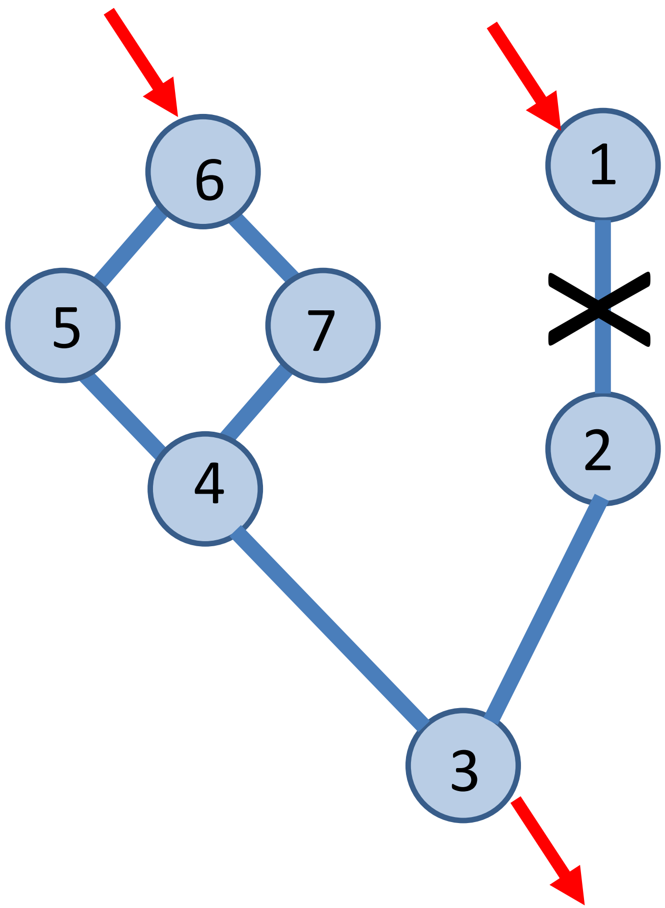




Dephasing & Durability

Up till now: analysis driven by power output

The biologists' intuition: its all about ***stability*** and ***Durability***



$$R_{1\leftrightarrow 2} = \frac{\dot{Q}_{out}(no\ link)}{\dot{Q}_{out}}$$

Dephasing & Durability

Up till now: analysis driven by power output

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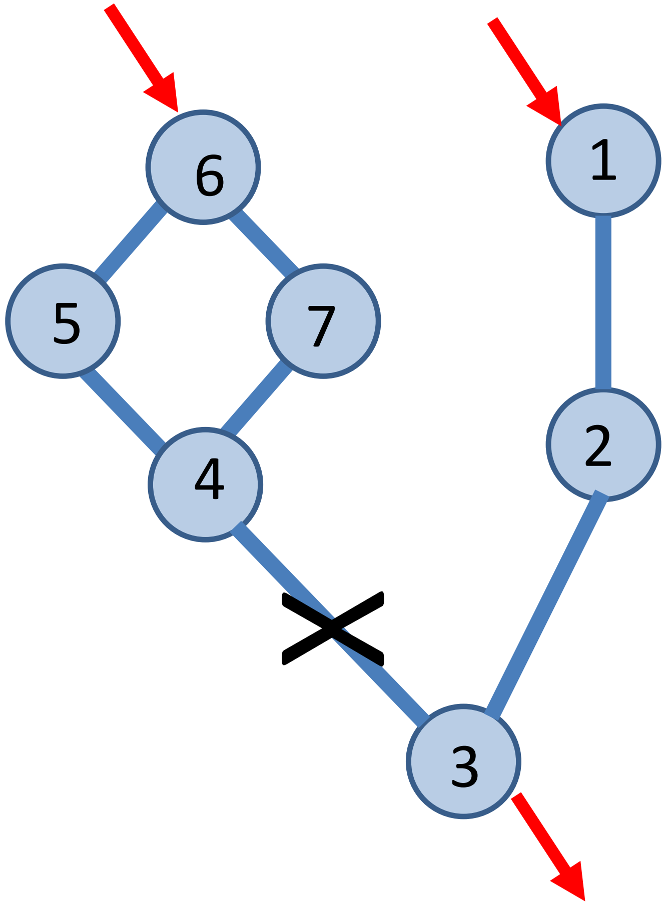
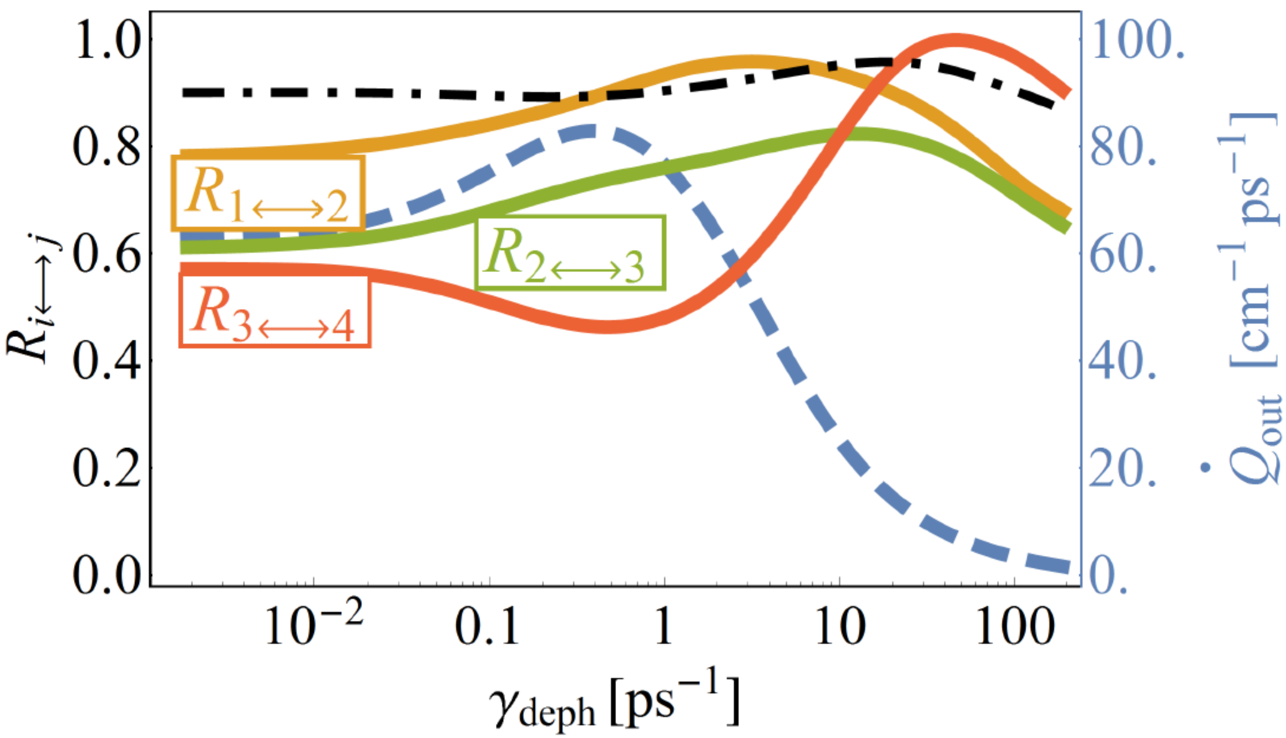


$$R_{3\leftrightarrow 4} = \frac{\dot{Q}_{out}(no\ link)}{\dot{Q}_{out}}$$

Dephasing & Durability

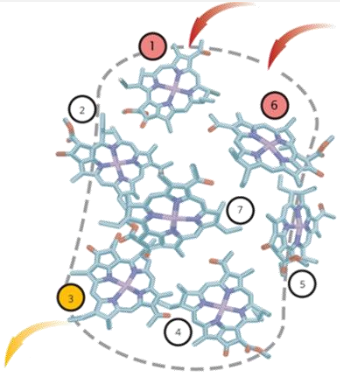


Conclusion: dephasing does not assist durability

Hypothesis: the two-branch structure developed to aid durability. The "right amount" of dephasing evolved to optimize power output, **given the two-branch structure.**

Summary [*J. Phys. Chem. C*, **DOI:** 10.1021/acs.jpcc.5b08493]

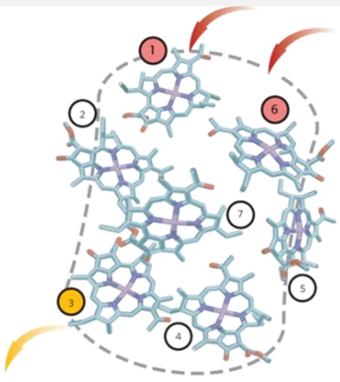
- A new approach to excitonic energy transfer: Calculating heat currents

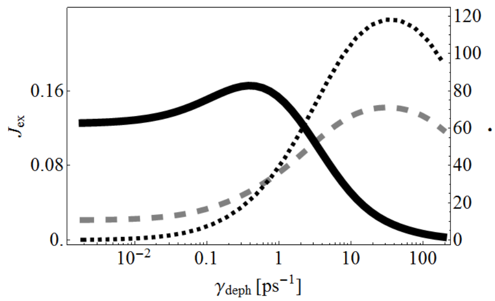


Summary [*J. Phys. Chem. C*, **DOI:** 10.1021/acs.jpcc.5b08493]

- A new approach to excitonic energy transfer: Calculating heat currents

- There is an optimal depahsing time for which **power output is maximal**





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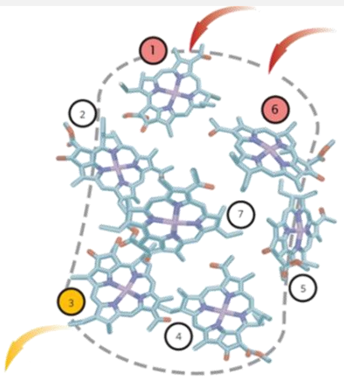

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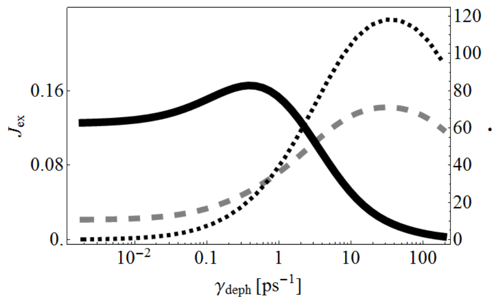
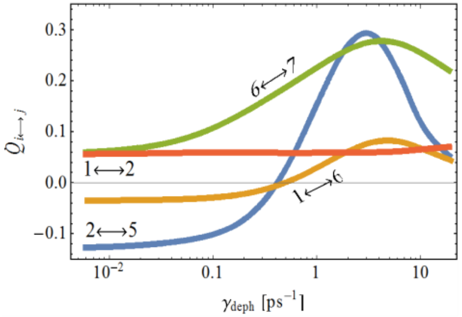


- This is due to *Directed Heat Flow*: the interplay between classical and quantum heat currents forces heat to flow along the branches



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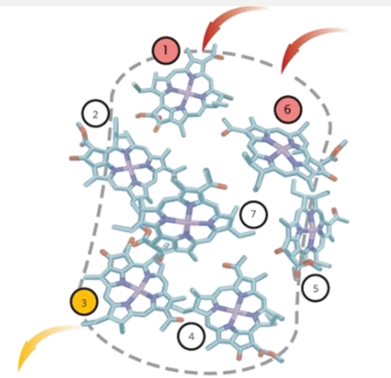

- A new approach to excitonic energy transfer:
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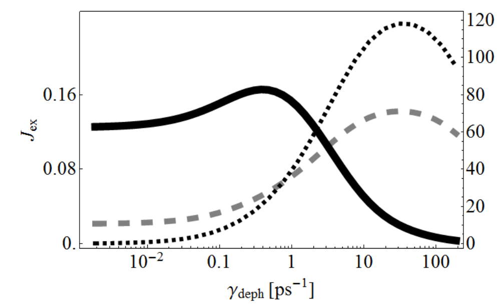

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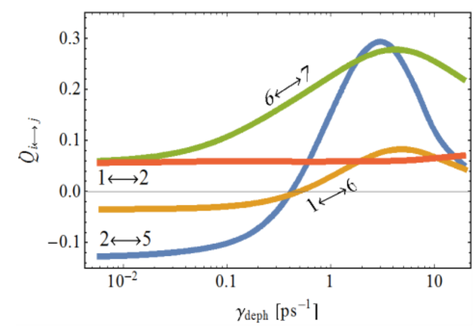

Thank you for our attention…

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Thanks to the organizers…