

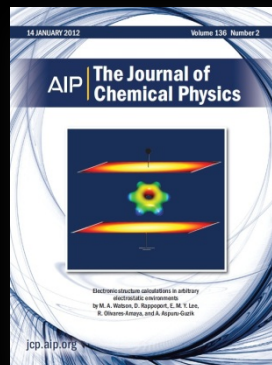
Quantum coherence

IN PHOTOSYNTHETIC LIGHT-HARVESTING COMPLEXES

Alán Aspuru-Guzik
Department of Chemistry and Chemical Biology
Harvard University

Quantum Computing for Chemistry

Nat Comm	3:882 (2012)
Nat Comm	3:880 (2012)
Nat Phys	8:285 (2012)
PNAS	109:754 (2012)
Nat Chem	2:106 (2010)
PNAS	105:18681 (2008)



Electronic Structure

PNAS	109:13928 (2012)
JCP	136:024101 (2012)
PRL	107:183002 (2011)
PRL	106:156405 (2011)
JPCL	1:2740 (2010)
PRL	104:043001 (2010)

Aspuru-Guzik Group 2006 – 2013

Organic Photovoltaics

Nature	480:504 (2011)
Ener Envir Sci	4:4849 (2011)
JPCL	2:2241 (2011)
Nat Comm	2:437 (2011)



Excitonics

JPCL	3:2357 (2012)
Biophys J	102:649 (2012)
PNAS	108:17615 (2011)
PNAS	108:16521 (2011)
NJP	11:033003 (2009)
JCP	129:174106 (2008)

Quantum mechanical effects

IN CHEMISTRY... AND BIOLOGY?

AGGREGED UPON CLASSICAL DYNAMICS

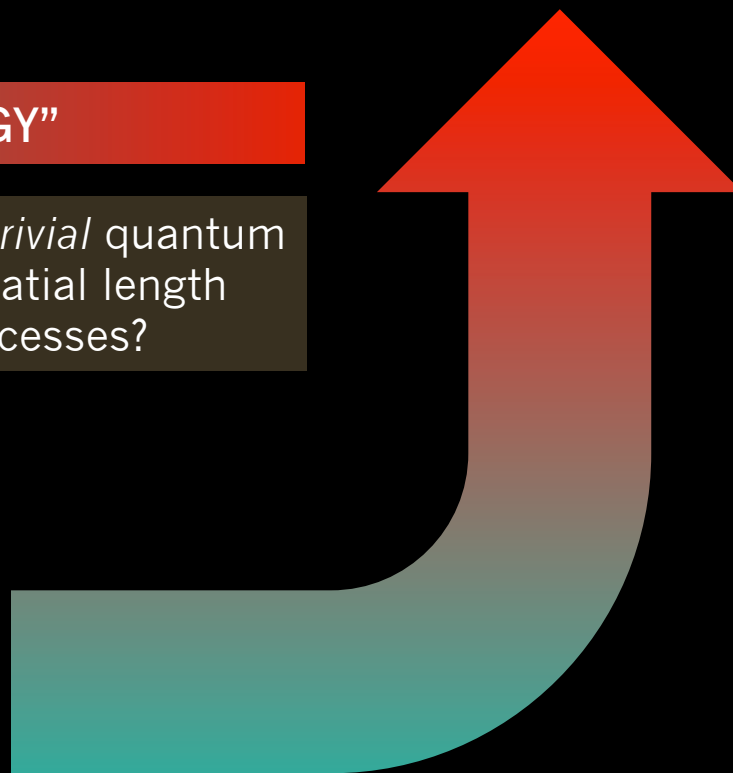
Motion of proteins in e.g. molecular motors...
Milliseconds, tens of nanometers

"QUANTUM BIOLOGY"

Are there processes where *non-trivial* quantum effects at *non-trivial* time and spatial length scales relevant to biological processes?

MANIFESTLY QUANTUM EFFECTS

Coherent superposition of atomic wave functions in conjugated molecules and in bonds in general.
~1 nm, femtoseconds



Quantum mechanical effects

IN CHEMISTRY... AND BIOLOGY?

“QUANTUM BIOLOGY”

Are there processes where *non-trivial* quantum effects at *non-trivial* time and spatial length scales relevant to biological processes?

Light-harvesting in photosynthesis
Fleming, Engel, Scholes, Moran, ...

Today

Vibrational effects in smell *hypothesis*
Turin, ...

?

Bird navigation: radical ion pair *hypothesis*
Schulten, Ritz, Hore, ...

?

The Brain
Penrose, ...

!?!? Sorry,
I don't buy this

Light-harvesting in photosynthesis Fleming, Engel, Scholes, Moran, ...

Observation: Long-lived (~ 1 ps) coherent superposition of exciton states
In photosynthetic complexes upon laser excitation in ultrafast experiments

Questions: Do these suggest non-trivial quantum transport in photosynthesis? Could they be relevant to function?

Talk outline

What do you mean by coherence?

What is an exciton?

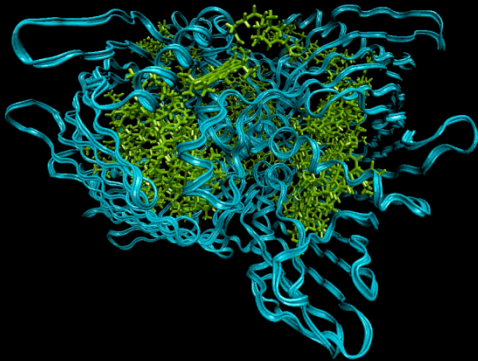
Coherent quantum beats by 2D ultrafast spectroscopy

Design of molecular quantum process tomography

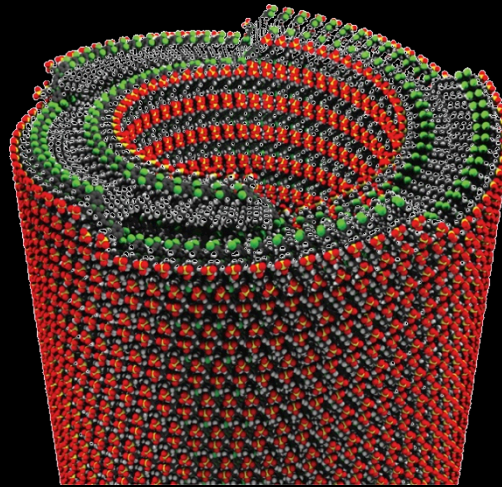
Coherence in green-sulfur bacteria

Molecular aggregates

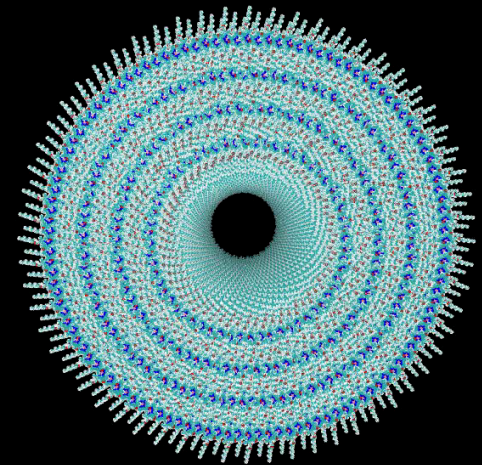
EXCITONIC SYSTEMS EXAMINED IN THIS TALK



Fenna-Mathews-Olson
complex (FMO)



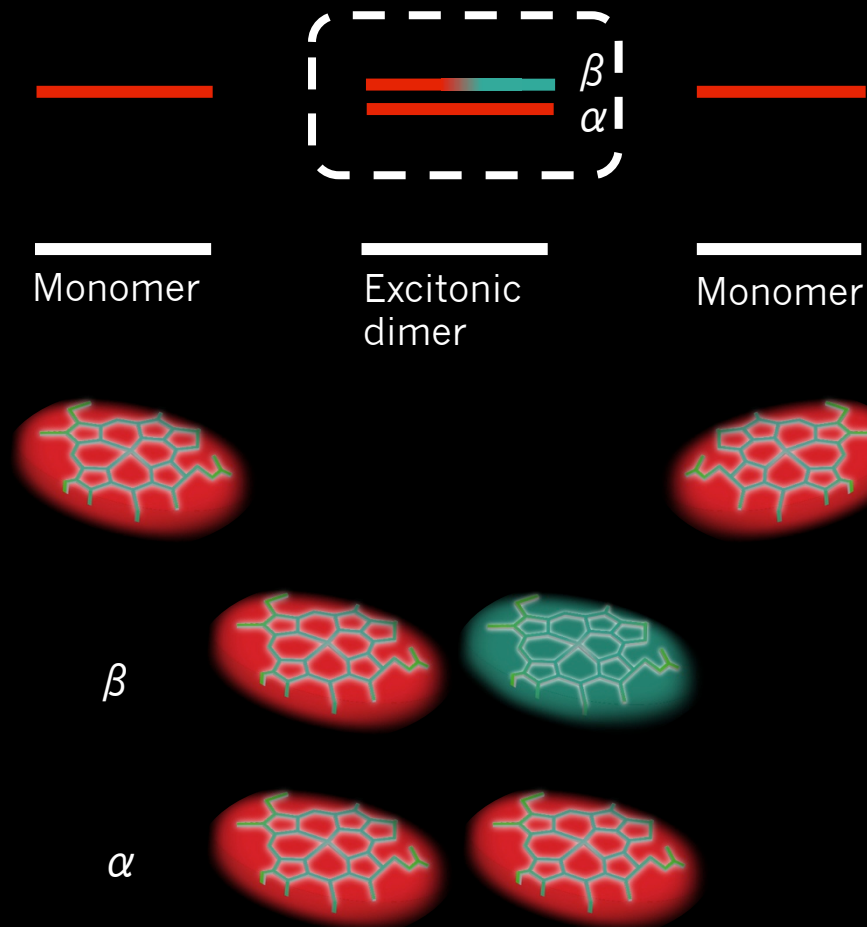
Double-walled
cyanine J-aggregate



Chlorosome antenna

What is an exciton?

EXAMPLE: BACTERIOCHLOROPHYLLS IN A PHOTOSYNTHETIC COMPLEX



$$d \sim 1 - 100 \text{ \AA}$$

$$V_{12} \sim 1 - 100 \text{ cm}^{-1}$$

$$kT = 208 \text{ cm}^{-1} (300\text{k}),$$
$$= 53 \text{ cm}^{-1} (77\text{k})$$

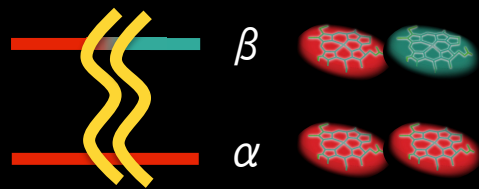
Temporal quantum coherence

QUANTUM COHERENCE

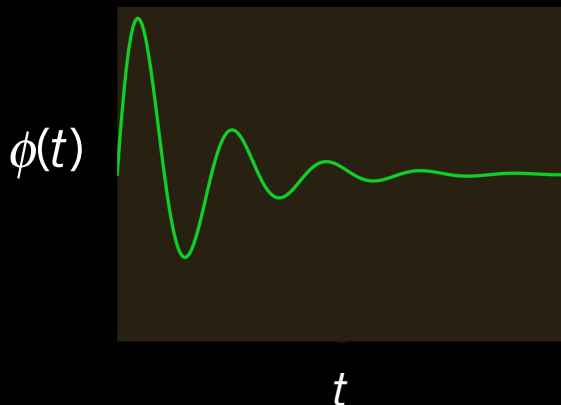
Quantum coherence is the preservation of phase relations in superpositions of two or more quantum states.

DECOHERENCE

The loss of quantum coherence due to the interaction of the system with its environment.



$$|\Psi(0)\rangle = \frac{1}{\sqrt{2}} \left(|\text{red spheres}\rangle + e^{i\phi} |\text{green spheres}\rangle \right)$$



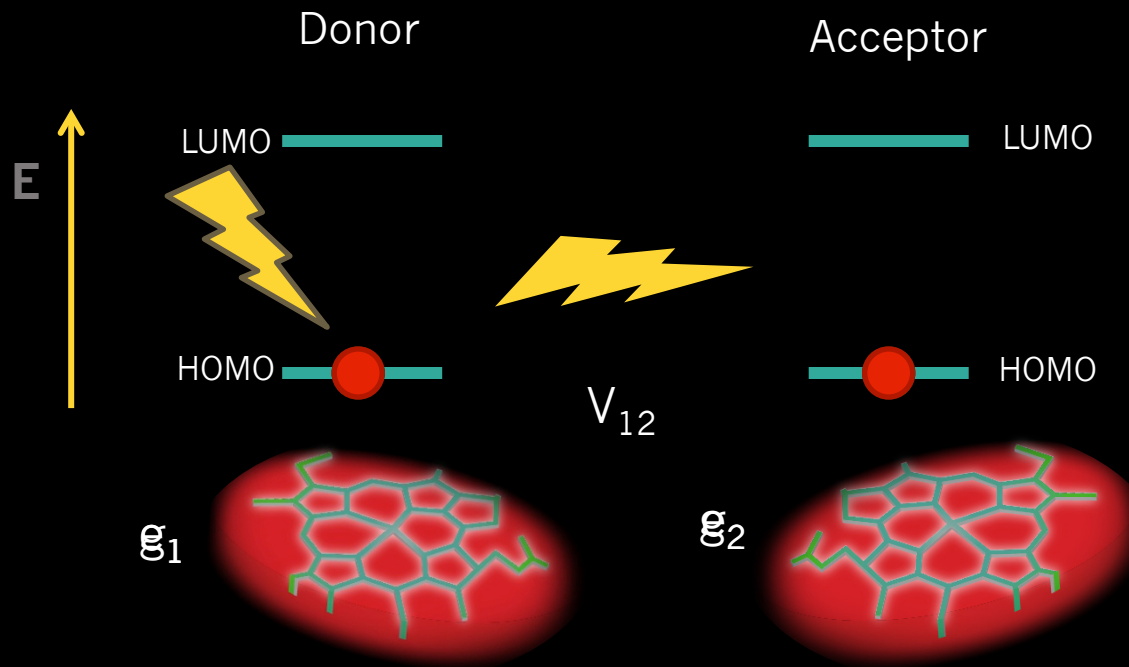
$$\rho(0) = \frac{1}{2} \begin{pmatrix} 1 & e^{i\phi} \\ e^{-i\phi} & 1 \end{pmatrix} \rightarrow \rho(T) = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

QUANTUM

CLASSICAL

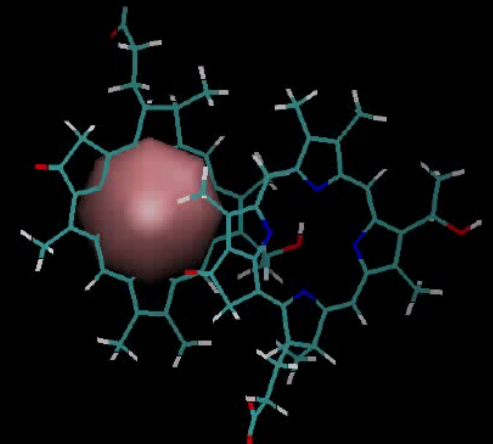
Exciton transfer

COHERENT VS INCOHERENT ENERGY TRANSFER

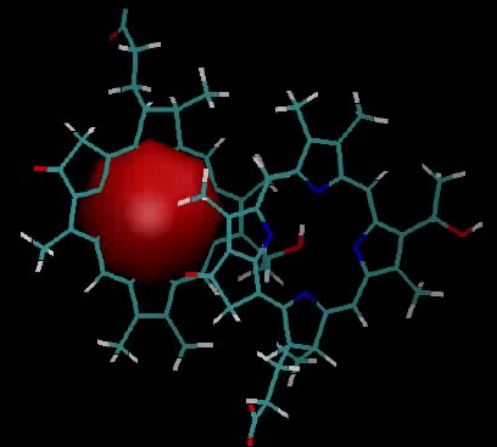


Incoherent – Förster (FRET) / Dexter
(classical transport)

Coherent – CRET
(quantum transport)



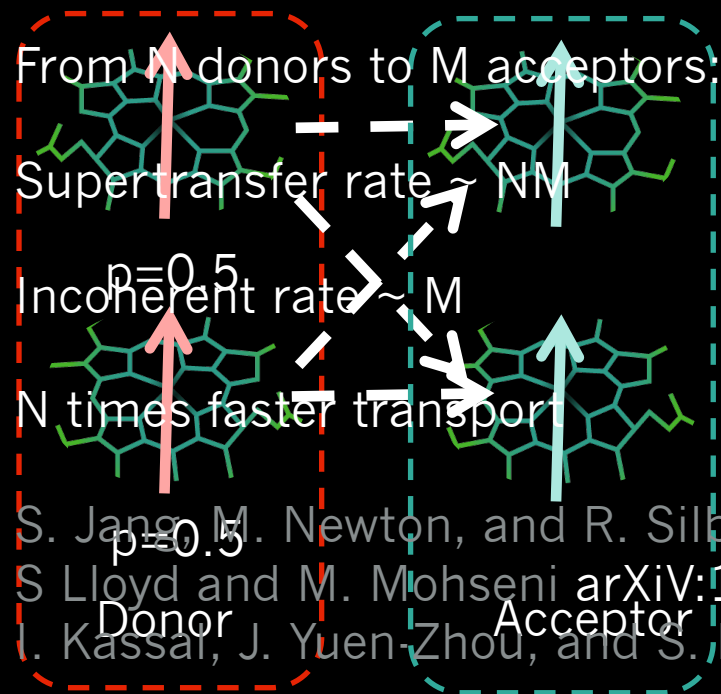
Incoherent



Coherent

Supertransfer: Spatial coherence

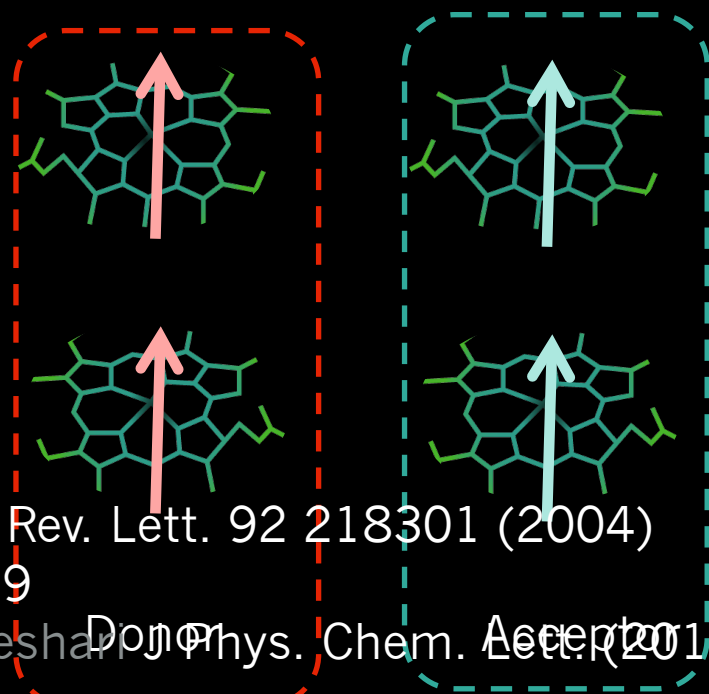
MULTICHROMOPHORIC RESONANCE ENERGY TRANSFER



S. Jang, M. Newton, and R. Silbey Phys. Rev. Lett. 92 218301 (2004)

S Lloyd and M. Mohseni arXiv:1005.2579

I. Kassal, J. Yuen-Zhou, and S. Rahimi-Keshari Phys. Chem. Chem. Lett. (2013)



$$\gamma \propto |\mu_D \mu_A|^2 = \mu^4$$

$$\mu_D = \frac{\mu_1 + \mu_2}{\sqrt{2}}$$

$$\mu_A = \frac{\mu_3 + \mu_4}{\sqrt{2}}$$

Incoherent rate $\Gamma_{incoh} \propto 2\mu^4$

$$\Gamma_{coh} \propto \left[\left(\frac{\mu + \mu}{\sqrt{2}} \right)_D \left(\frac{\mu + \mu}{\sqrt{2}} \right)_A \right]^2 = 4\mu^4$$

Coherently-delocalized rate

Supertransfer: Spatial coherence

MULTICHROMOPHORIC RESONANCE ENERGY TRANSFER

From N donors to M acceptors:

Supertransfer rate $\sim NM$

Incoherent rate $\sim M$

N times faster transport

S. Jang, M. Newton, and R. Silbey Phys. Rev. Lett. 92 218301 (2004)

S Lloyd and M. Mohseni arXiv:1005.2579

I. Kassal, J. Yuen-Zhou, and S. Rahimi-Keshari J Phys. Chem. Lett. (2013)

$$\gamma \propto |\mu_D \mu_A|^2 = \mu^4$$

Incoherent rate $\Gamma_{incoh} \propto 2\mu^4$

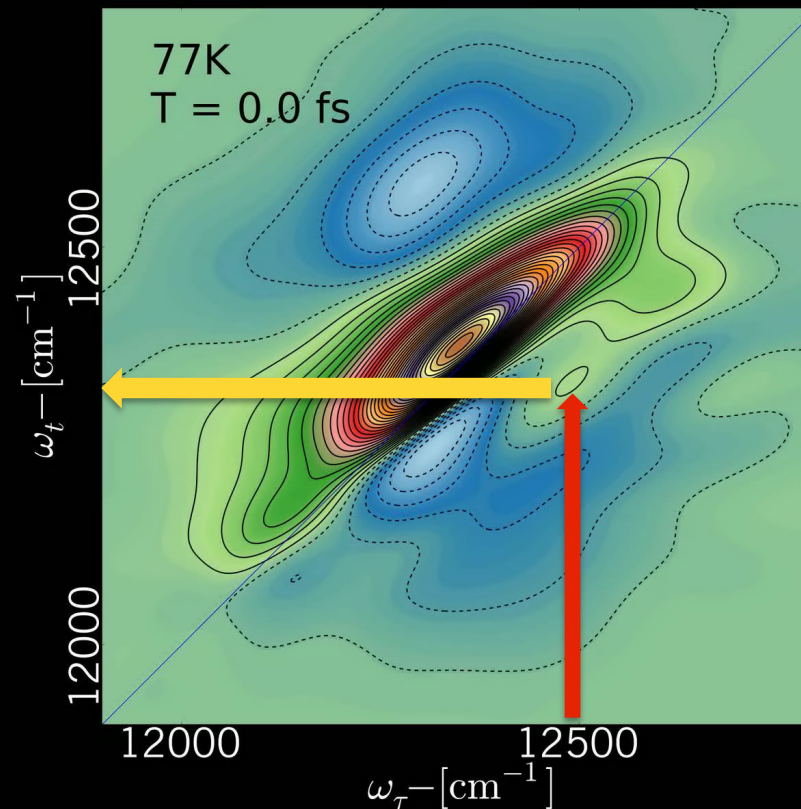
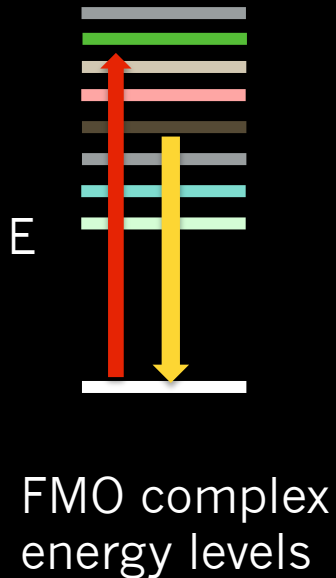
$$\mu_D = \frac{\mu_1 + \mu_2}{\sqrt{2}} \quad \mu_A = \frac{\mu_3 + \mu_4}{\sqrt{2}}$$

$$\Gamma_{coh} \propto \left[\left(\frac{\mu + \mu}{\sqrt{2}} \right)_D \left(\frac{\mu + \mu}{\sqrt{2}} \right)_A \right]^2 = 4\mu^4$$

Coherently-delocalized rate

Observed long-lived oscillations

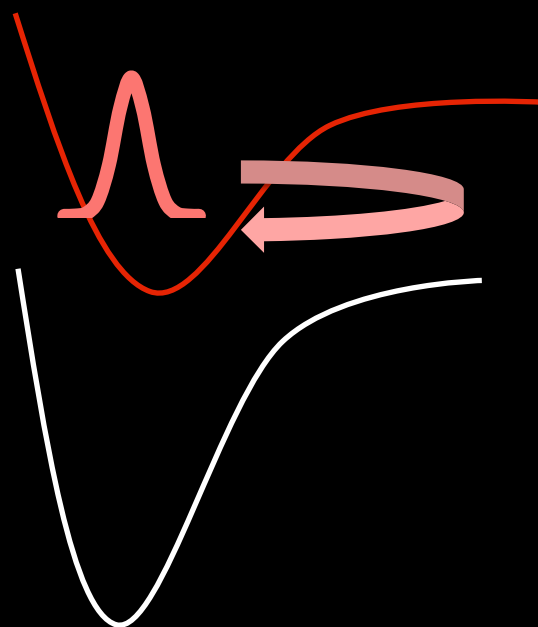
BY MEANS OF 2D SPECTROSCOPY



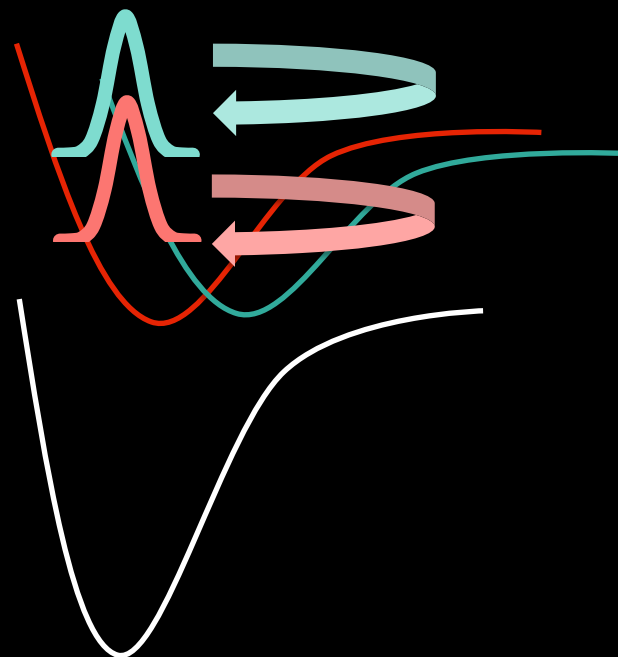
Experiments: Fleming et al., Nature 447, 782 (2007) Engel et al., Proc. Nat. Acad. Sci. 107, 12766 (2010)
Other systems: Scholes et al., Science 323, 329 (2009) Fleming et al., Nat. Chem. 4, 389 (2012)

Coherences

VIBRATIONAL AND ELECTRONIC



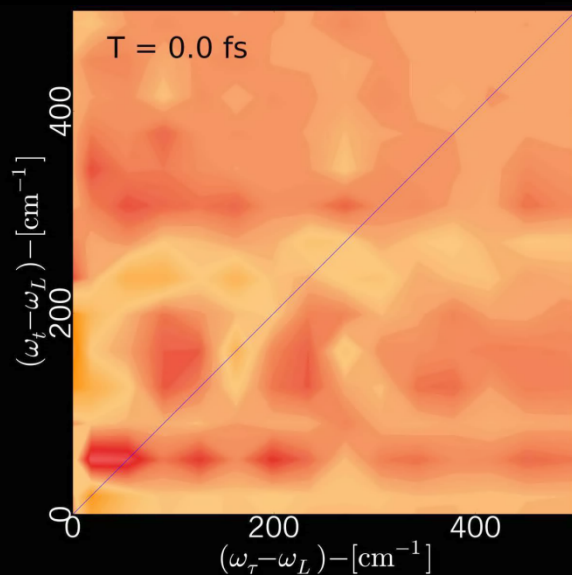
VIBRATIONAL COHERENCE



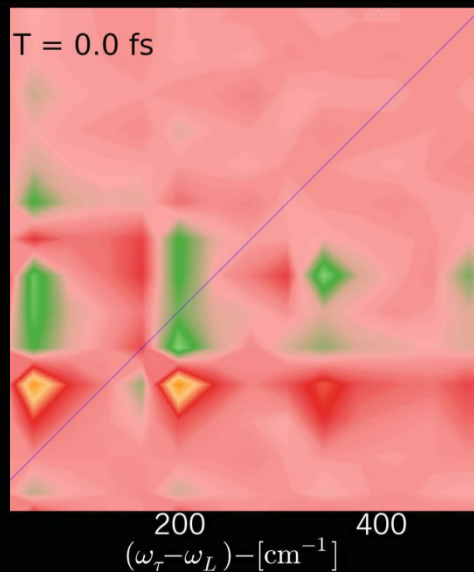
ELECTRONIC COHERENCE

Cross-peak oscillations

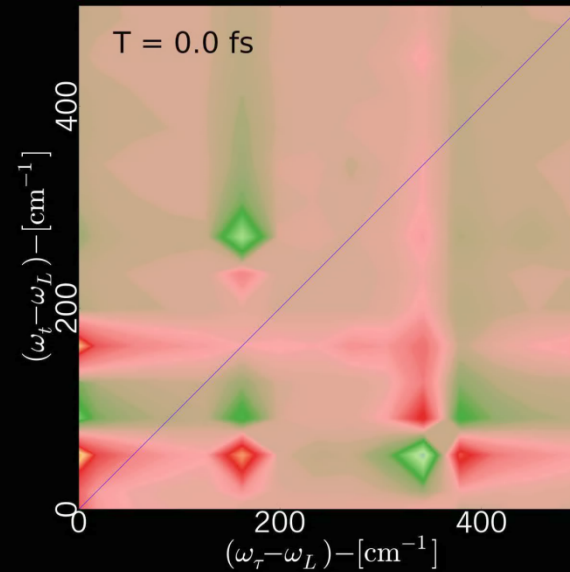
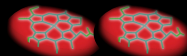
VIBRATIONAL AND ELECTRONIC



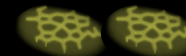
MONOMER



COHERENT DIMER



INCOHERENT DIMER



J. Yuen-Zhou, J. Krich, and A. Aspuru-Guzik, J. Chem. Phys. 136, 234501 (2012)

On theory and experiment

EXTRACTING THE FULL QUANTUM DYNAMICS

DIRECT SIMULATION

Model 1



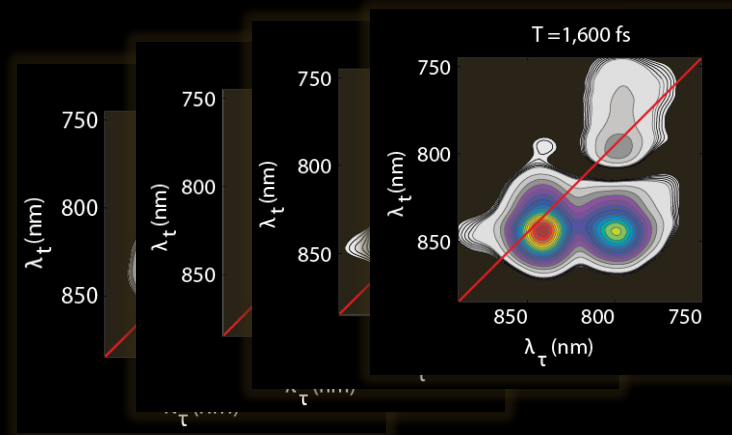
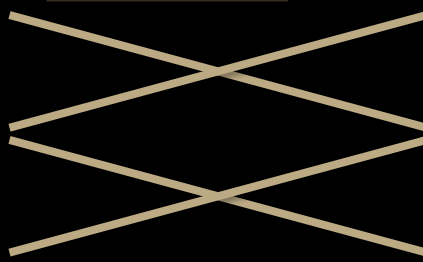
Model 2



Model 3



Model 1



QUANTUM TOMOGRAPHY

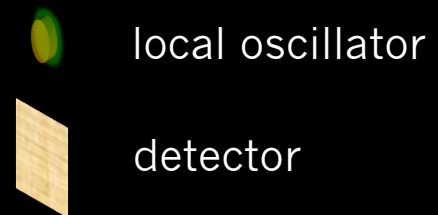
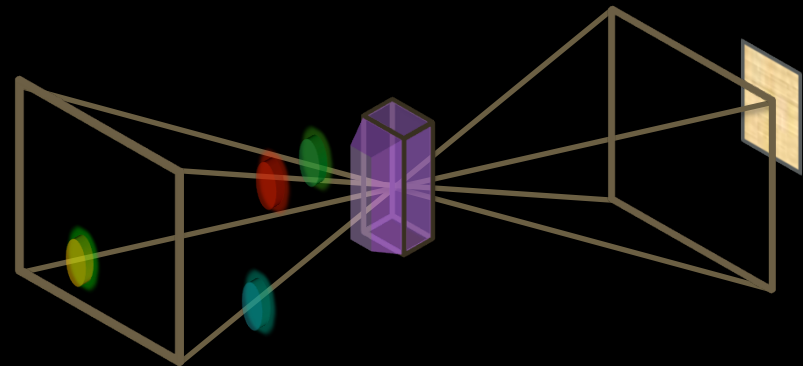
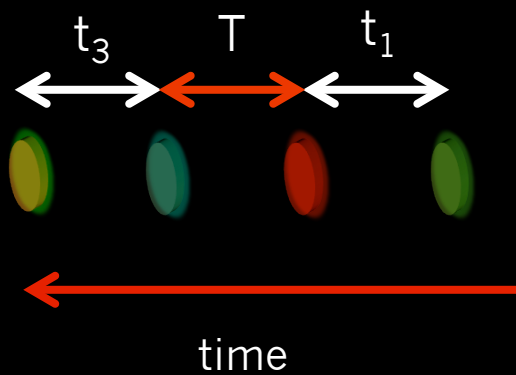


SYSTEM DYNAMICS

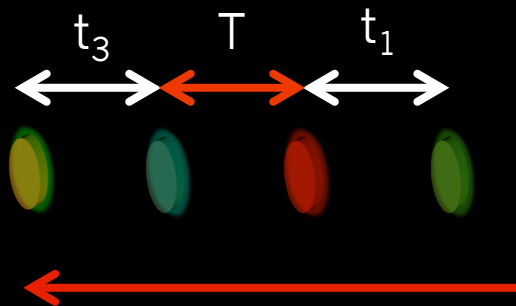
J. Yuen-Zhou, J. Krich, M. Mohseni, A.A.-G., Proc. Nat. Acad. Sci. (2012);

J. Yuen-Zhou and A. A.-G., J. Chem. Phys. (2011); J. Yuen-Zhou, J. Krich., A. A.-G., J. Chem. Phys. (2012)

2D electronic spectroscopy 101

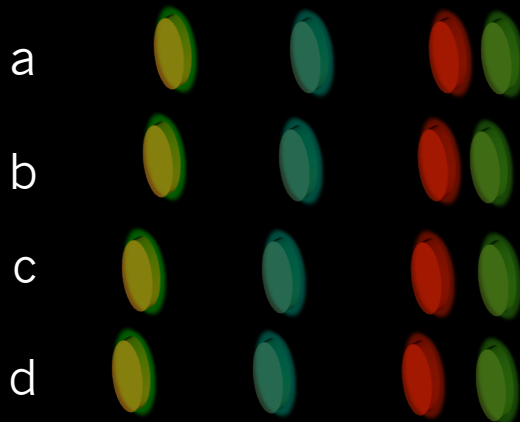


2D electronic spectroscopy 102



time

Experiments



...

1

Scan t_1 , T , t_3

2

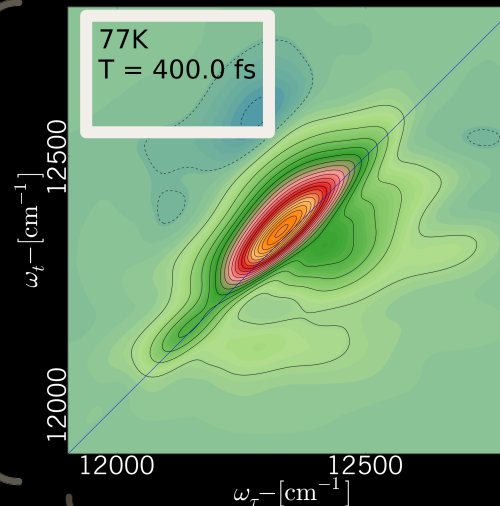
Fourier transform t_1 and t_3

3

Plot as a function of T

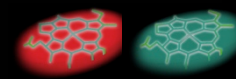
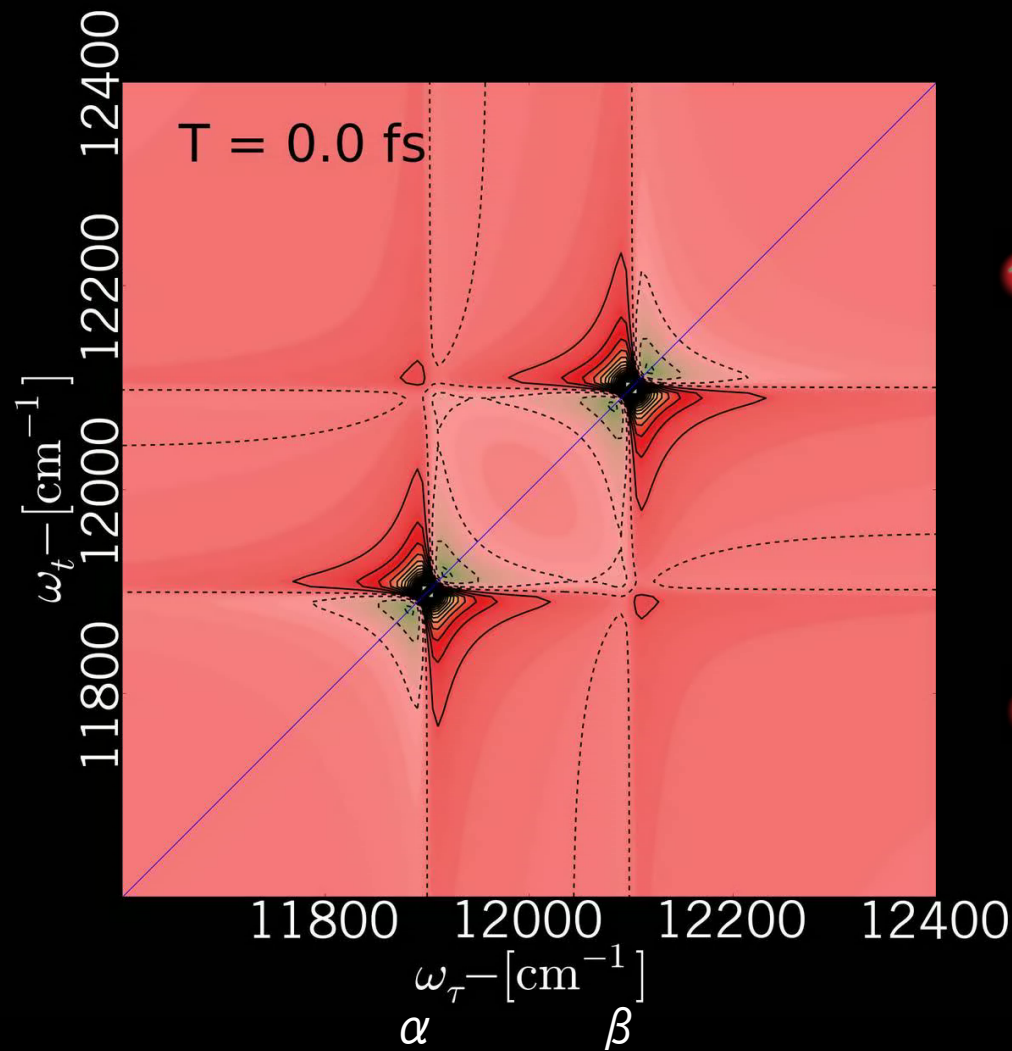
Population time

Fourier transform of t_3



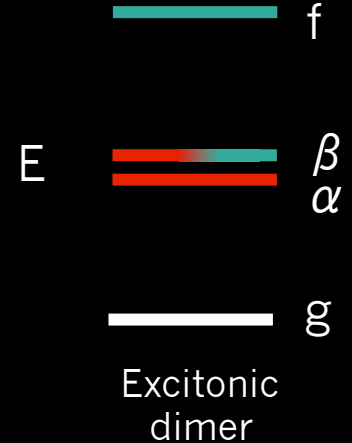
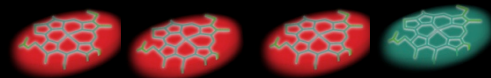
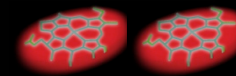
Fourier transform of t_1

Model dimer quantum beats



β

α



f – double excitation
 α, β – single excitons
 g – ground state

Quantum tomography

RECONSTRUCTING QUANTUM STATES AND THEIR DYNAMICS

QUANTUM STATE TOMOGRAPHY

Reconstruct the density matrix from measurements in different bases on multiple identical copies of a quantum state

QUANTUM PROCESS TOMOGRAPHY

Reconstruct the density matrix from measurements in different bases on multiple identical copies **for multiple initial states** of a quantum system

J. Yuen-Zhou, J. Krich, M. Mohseni, A. Aspuru-Guzik, Proc. Nat. Acad. Sci. 108, 17615 (2011)

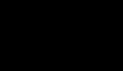
J. Yuen-Zhou and A. Aspuru-Guzik, J. Chem. Phys. 134, 134505 (2011)

J. Yuen-Zhou, J. Krich and A. Aspuru-Guzik, J. Chem. Phys. 136, 234501 (2012)

Systems identification

CLASSICAL PROCESS TOMOGRAPHY

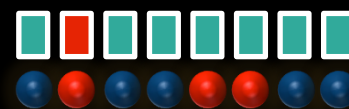
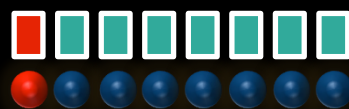
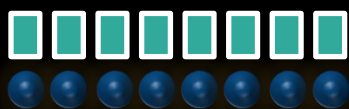
0
1



DIGITAL
CHIP

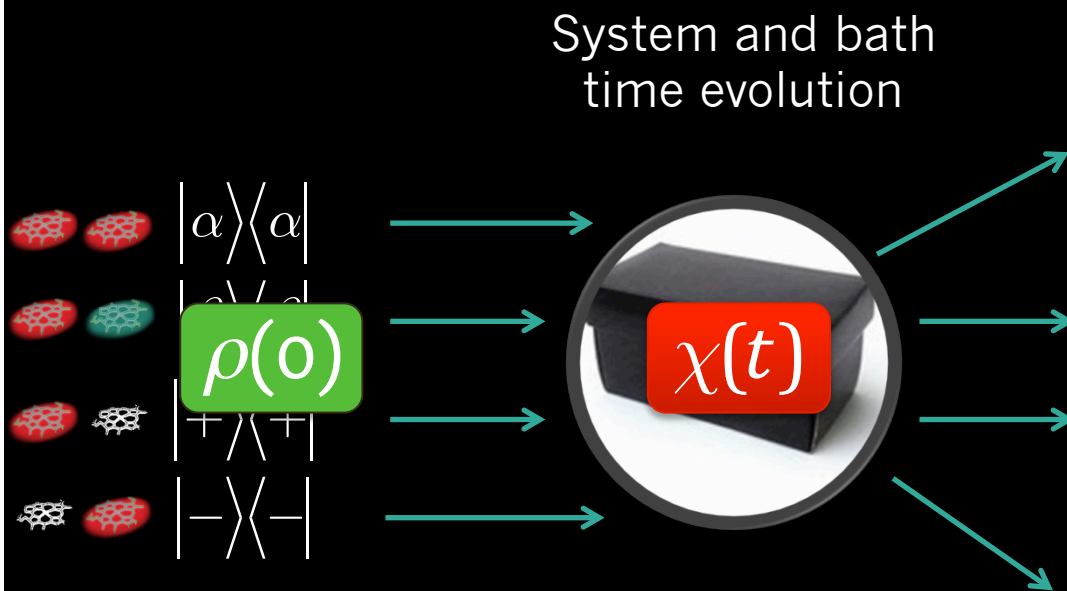
This will fully
characterize
the process
carried out by
the chip

Input
Output



... 2^8 experiments

Quantum process tomography



$$\begin{array}{cc} \langle \alpha | \rho_{\alpha}(T) | \alpha \rangle & \langle \alpha | \rho_{\beta}(T) | \alpha \rangle \\ \langle \beta | \rho_{\alpha}(T) | \beta \rangle & \langle \beta | \rho_{\beta}(T) | \beta \rangle \\ \langle + | \rho_{\alpha}(T) | + \rangle & \langle + | \rho_{\beta}(T) | + \rangle \\ \langle - | \rho_{\alpha}(T) | - \rangle & \langle - | \rho_{\beta}(T) | - \rangle \\ \langle \alpha | \rho_{+}(T) | \alpha \rangle & \langle \alpha | \rho_{-}(T) | \alpha \rangle \\ \langle \beta | \rho_{+}(T) | \beta \rangle & \langle \beta | \rho_{-}(T) | \beta \rangle \\ \langle + | \rho_{+}(T) | + \rangle & \langle + | \rho_{-}(T) | + \rangle \\ \langle - | \rho_{+}(T) | - \rangle & \langle - | \rho_{-}(T) | - \rangle \end{array}$$

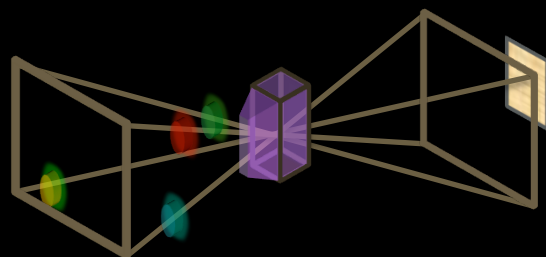
$$\rho(t) = \chi(t) \rho(0)$$

$$\rho_{cd}(t) = \sum_{ab} \chi_{cdab}(t) \rho_{ab}(0)$$

How much of ρ_{ab} made it to ρ_{cd} at time t ?

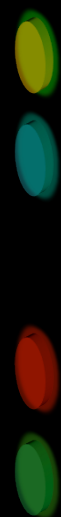
Quantum process tomography

USING ULTRAFAST SPECTROSCOPY



Chemistry ▶

◀ Quantum Information



echo
time (t_3)

population
time (T)

coherence
time (t_1)

detection

quantum
process

state
preparation

gg

$\rho(t)$

$\chi(t)$

$\rho(0)$

Spectroscopy as quantum process tomography

WHY IS IT IMPORTANT?

How much information is contained
in any spectroscopy experiment?

Can I arrange for many experiments to extract
the maximum amount of information?

What is impossible to know about the
chemical system?

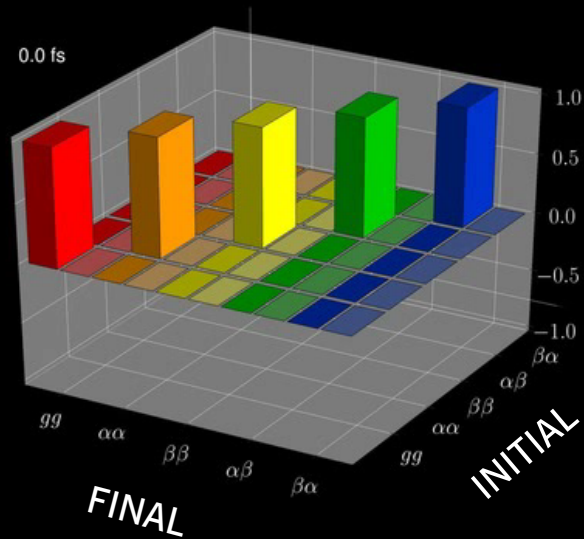
J. Yuen-Zhou, J. Krich, M. Mohseni, A. Aspuru-Guzik, Proc. Nat. Acad. Sci. 108, 17615 (2011)

J. Yuen-Zhou and A. Aspuru-Guzik, J. Chem. Phys. 134, 134505 (2011)

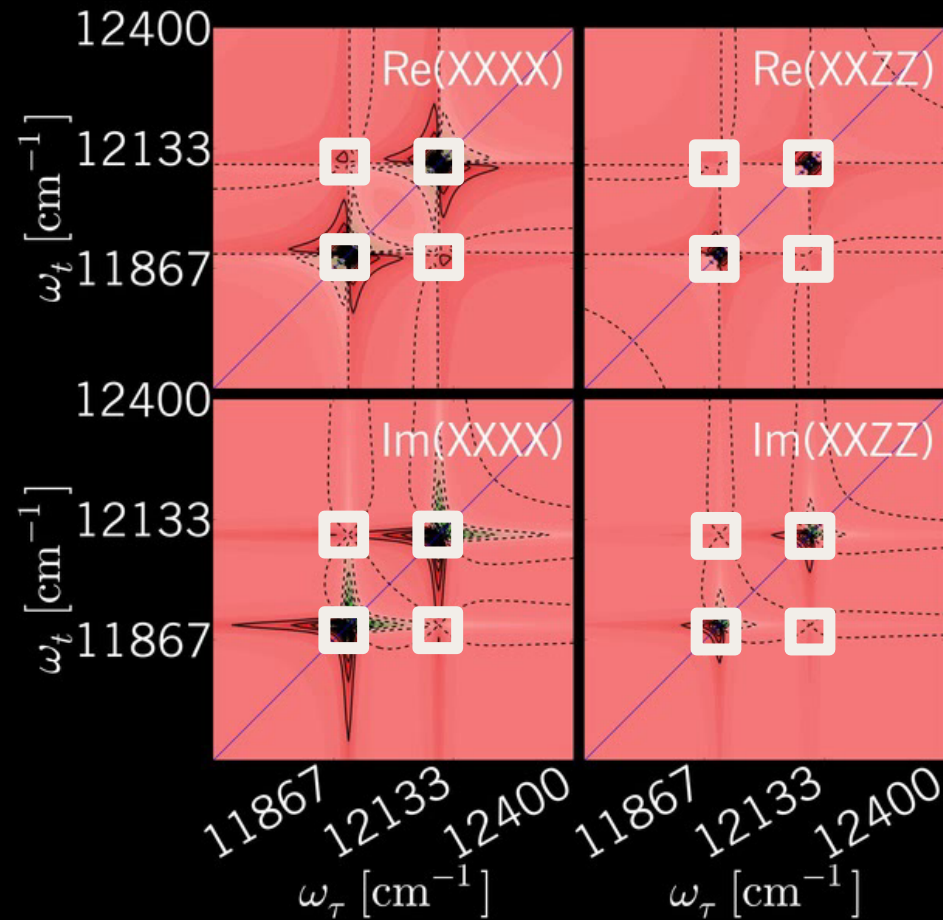
J. Yuen-Zhou, J. Krich and A. Aspuru-Guzik, J. Chem. Phys. 136, 234501 (2012)

Process tomography with 2D spectra

CHROMOPHORE HOMODIMER, CHANGING POLARIZATIONS



$\chi(t)$

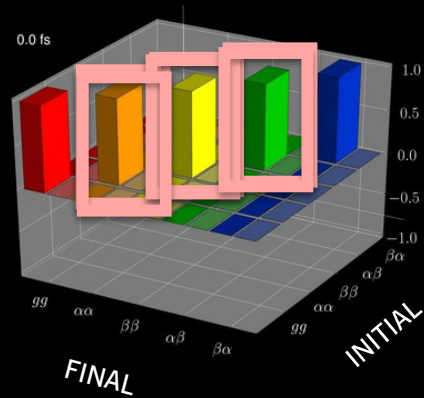


J. Yuen-Zhou, J. Krich, A. Aspuru-Guzik, J. Chem. Phys. 136, 234501 (2011)

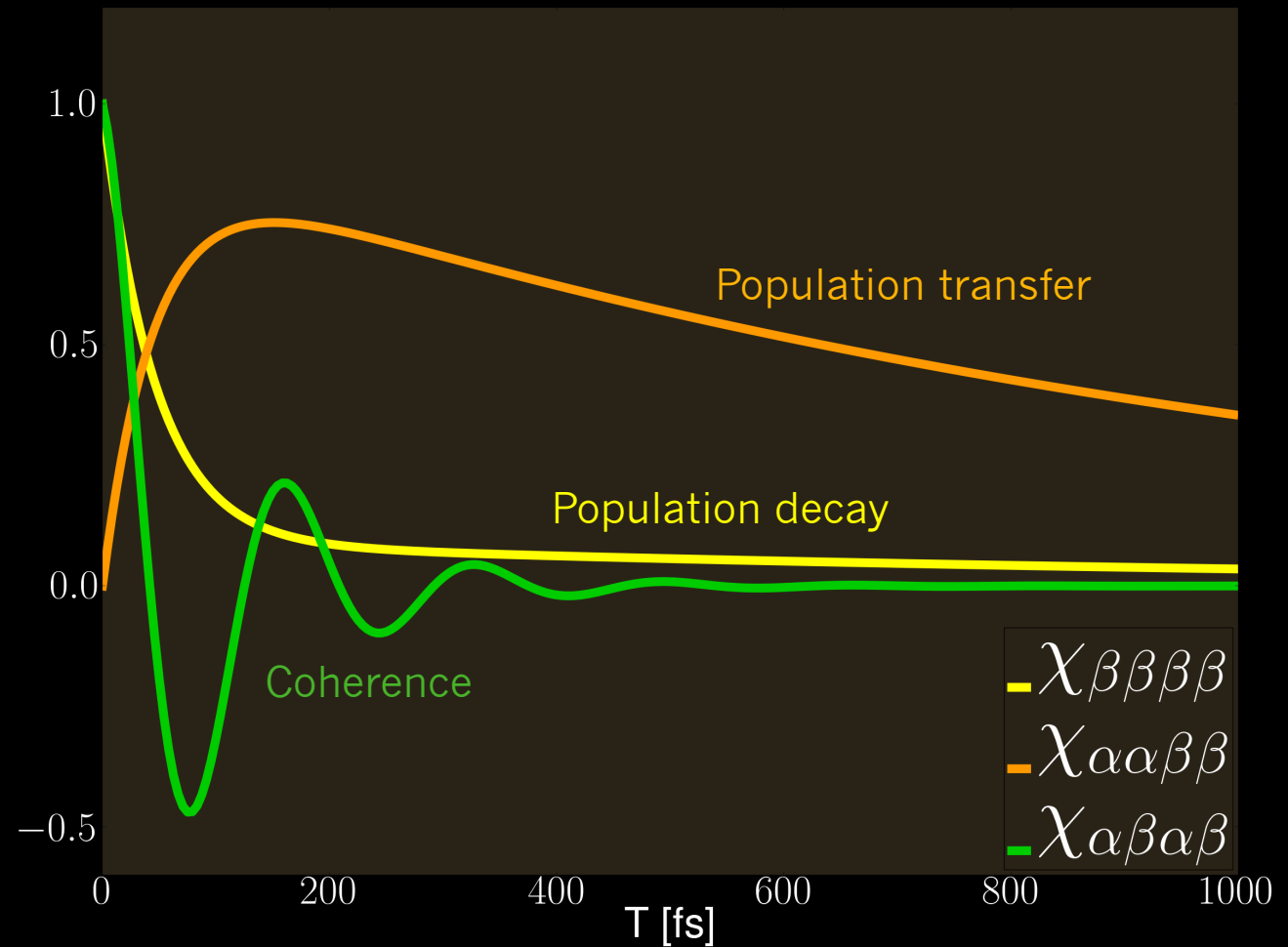
J. Yuen-Zhou, J. Krich, M. Mohseni, A.A.-G., Proc. Nat. Acad. Sci. 108, 17615 (2012)

Process matrix elements

HOW TO READ A PROCESS MATRIX

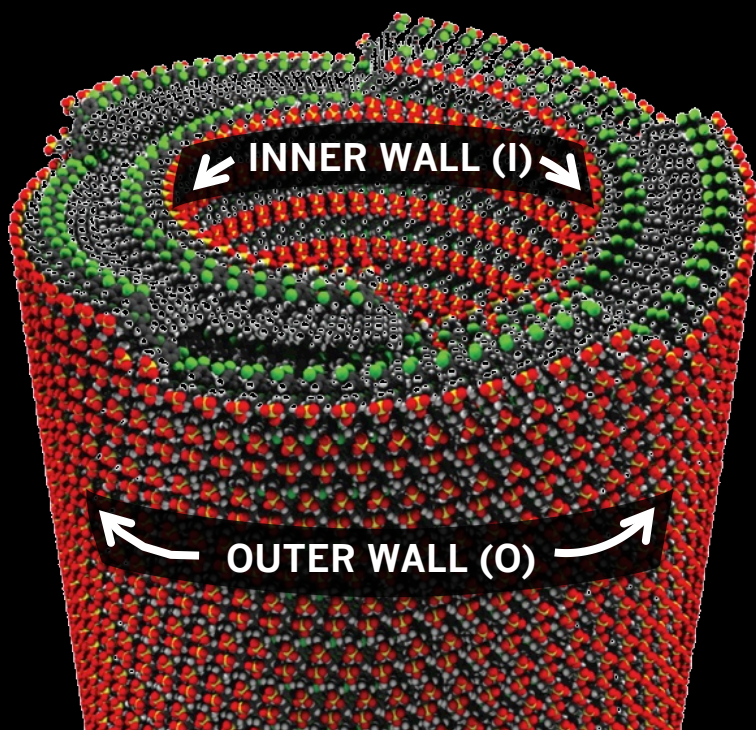
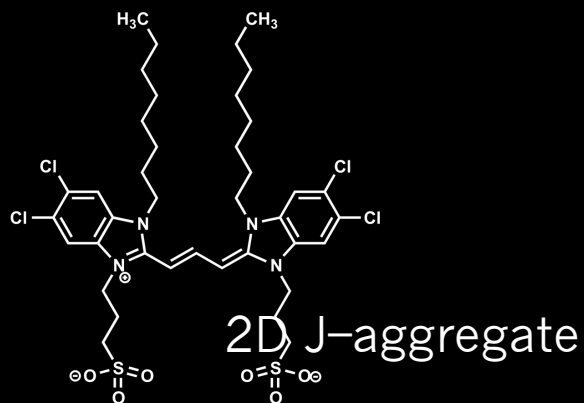


$\chi(t)$

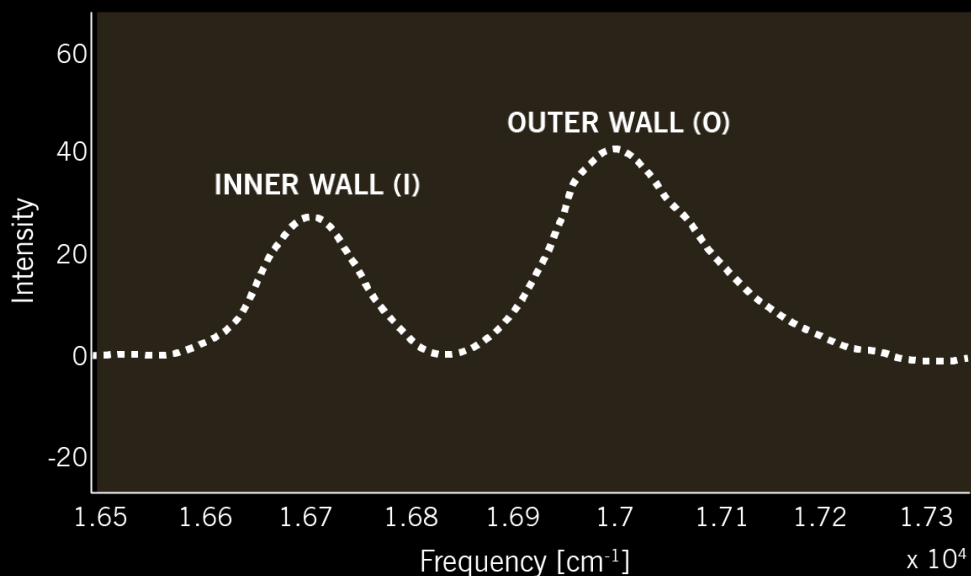


Artificial chlorosome

A SYSTEM FOR QUANTUM PROCESS TOMOGRAPHY



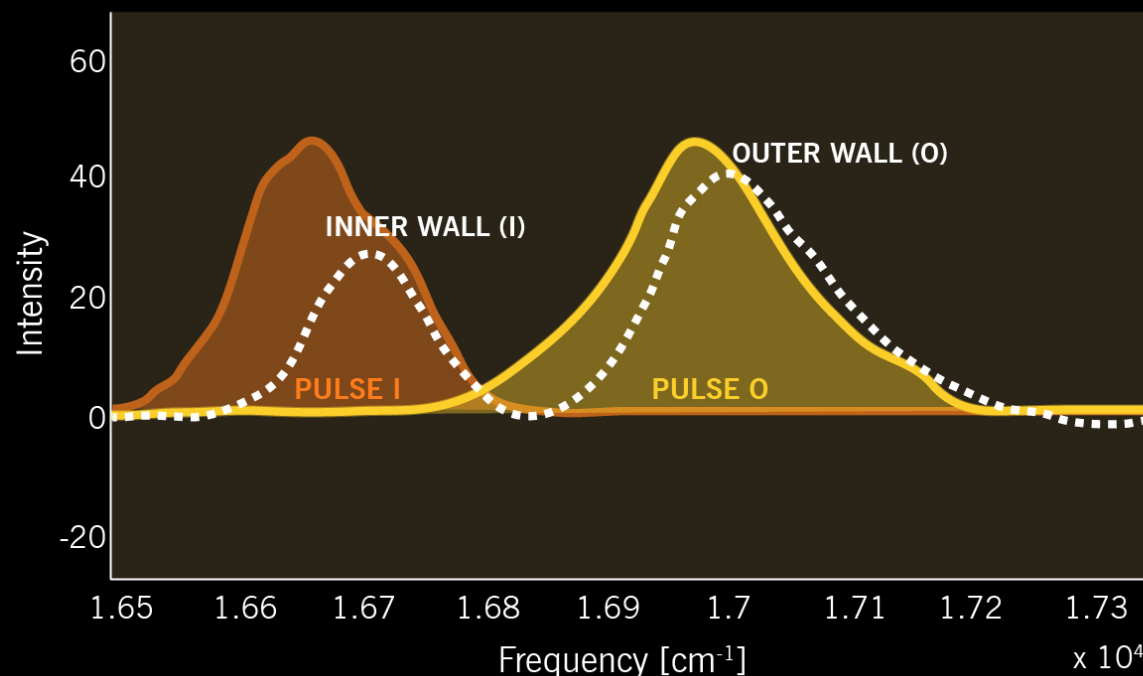
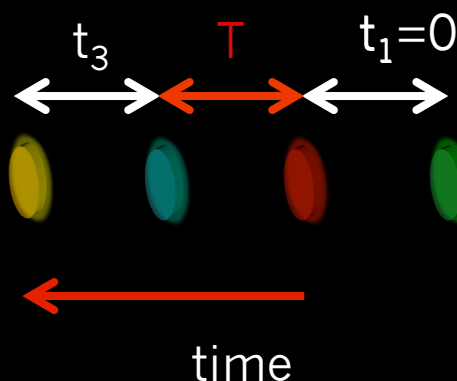
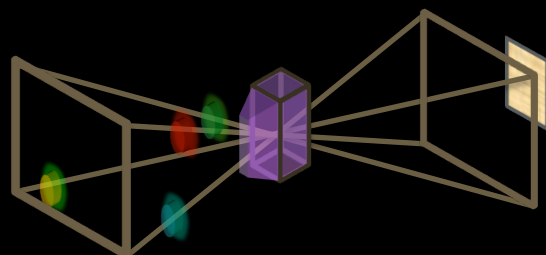
Chlorosome



Chlorosome: T. Fujita, J. Brookes, S. Saikin, A. Aspuru-Guzik, J. Phys. Chem. Lett. 3, 2357 (2012)
J-Aggregate: D. Eisele et al., Nature Chem. 4, 655 (2012)

Transient grating **process tomography**

FREQUENCY-RESOLVED APPROACH

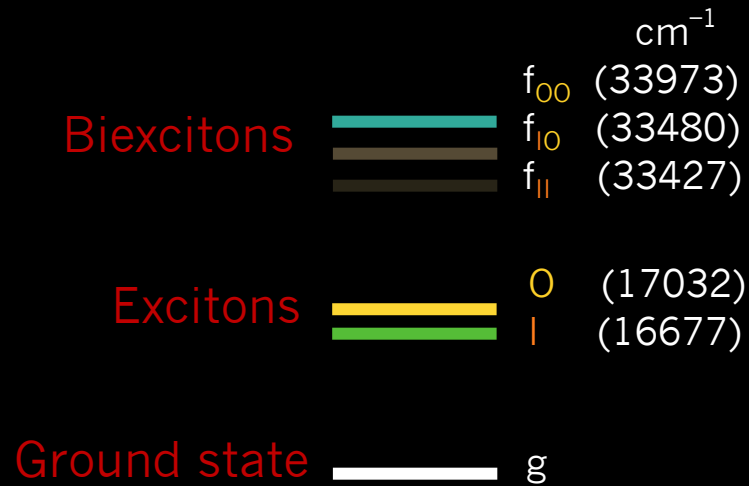


Narrowband pulses **I** and **O** address individual excitonic transitions
 8 different experiments (**III**, **OOO**, **IOI**, **OIO**, **IOO**, **OII**, **IIO**, **OOI**) / time point

J. Yuen-Zhou, J. Krich, A. Aspuru-Guzik (Harvard),
 Dylan Arias, Colby Steiner, Dorte Eisele, Mounqi Bawendi, Keith Nelson (MIT), Paper in Preparation.

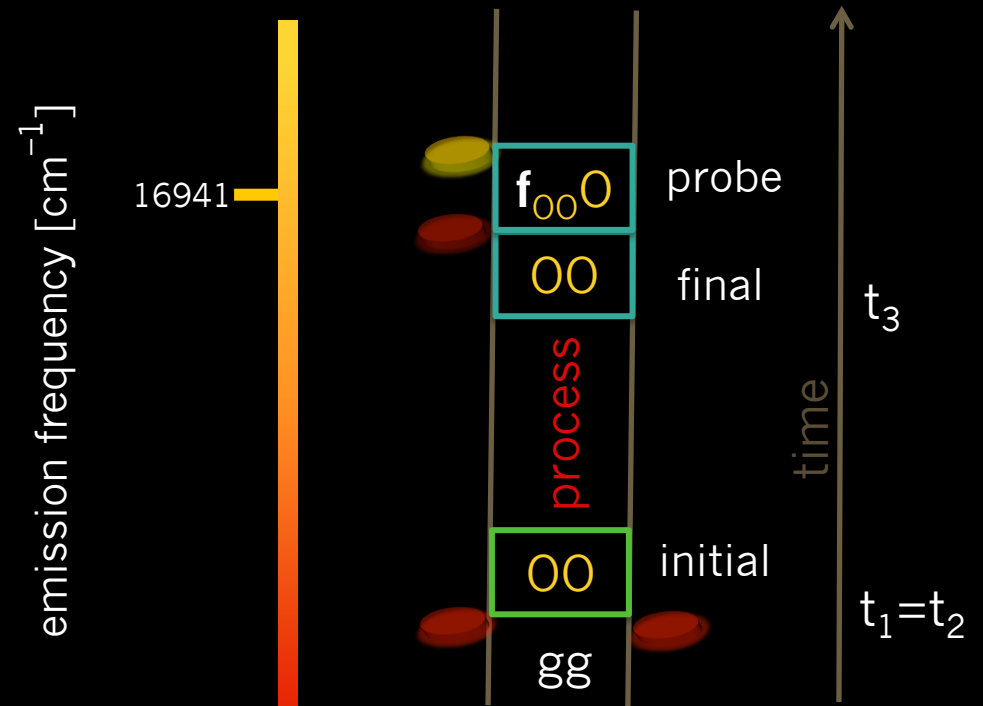
QPT measurement scheme

EXAMPLE: 000, ELEMENT $\chi_{0000}(T)$



Emission at $f_{00} - 0 = 16941 \text{ cm}^{-1}$

proportional to $\chi_{0000}(T) \text{ cm}^{-1}$
(population decay)

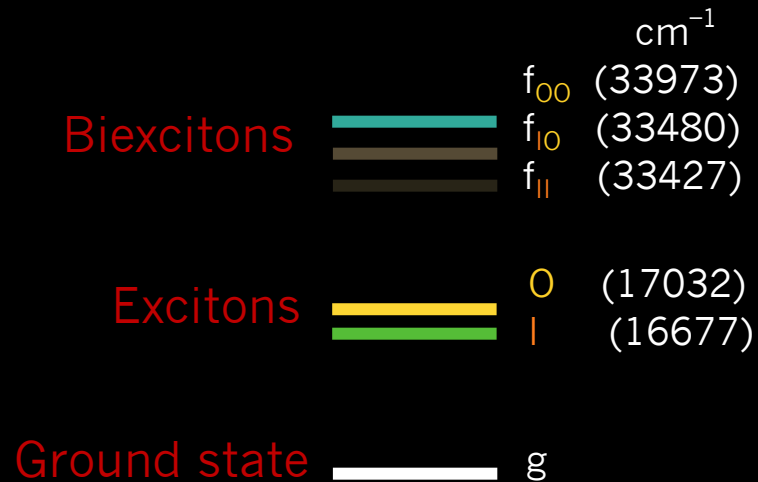


J. Yuen-Zhou, J. Krich, A. Aspuru-Guzik (Harvard),

Dylan Arias, Colby Steiner, Dorte Eisele, Mouni Bawendi, Keith Nelson (MIT), Paper in Preparation.

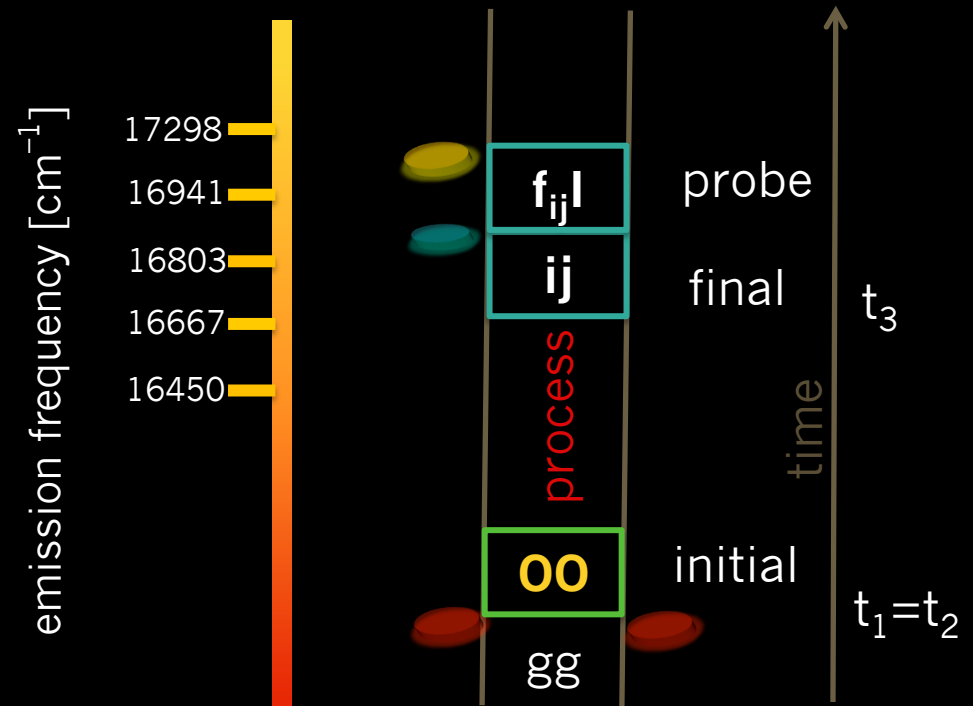
QPT measurement scheme

FOR ALL REMAINING ELEMENTS OF χ



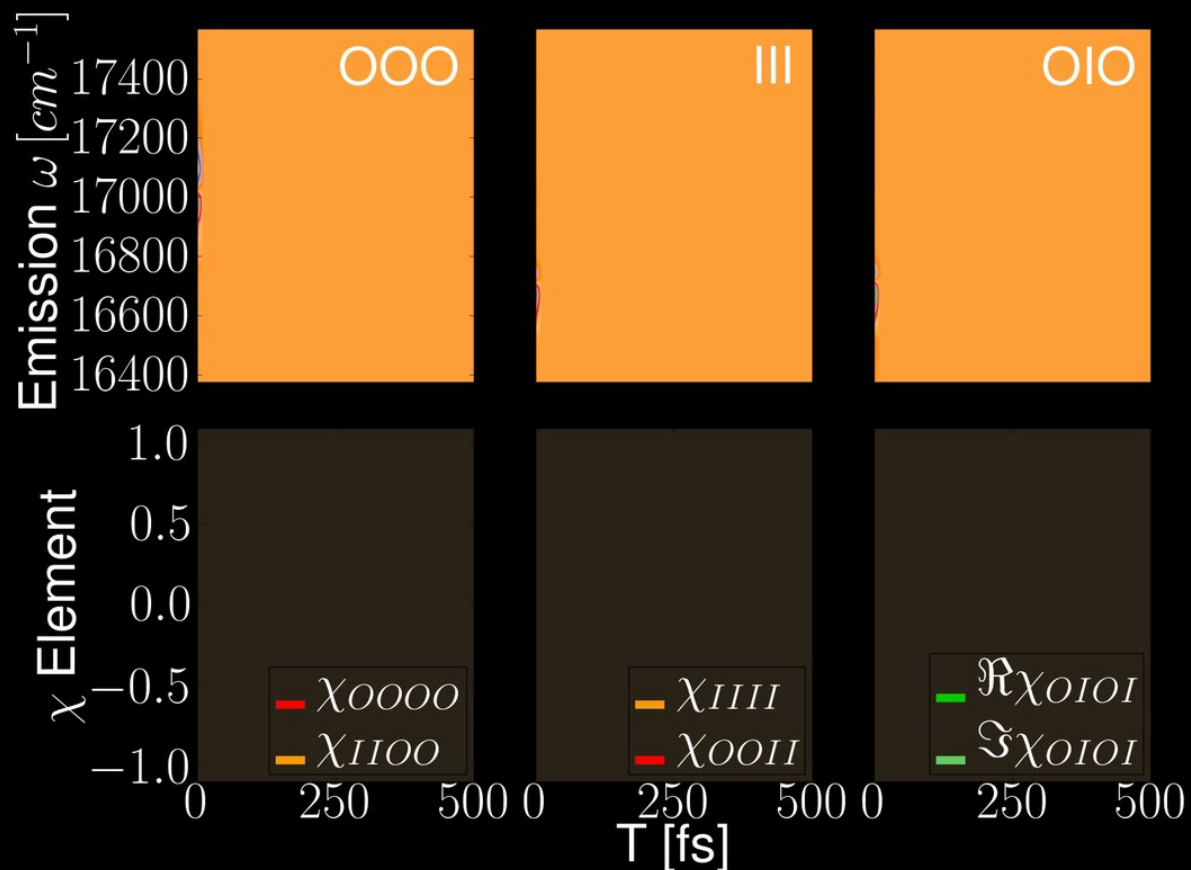
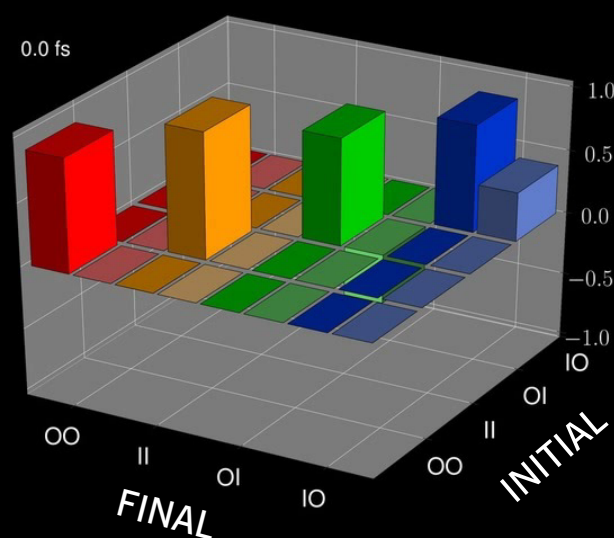
Emissions at $f_{ij} - j$

Proportional to additional elements of $\chi(T) \text{ cm}^{-1}$



First QPT experiment in chemistry

DOUBLE-WALLED J AGGREGATE (NELSON + ASPURU-GUZIK GROUPS)



J. Yuen-Zhou, J. Krich, A. Aspuru-Guzik (Harvard),
 Dylan Arias, Colby Steiner, Dorte Eisele, Mounqi Bawendi, Keith Nelson (MIT), Paper in Preparation.

Dynamics of J-aggregate

REVEALED BY QUANTUM PROCESS TOMOGRAPHY

Walls are coupled!

Coherence lifetime
of 200 fs

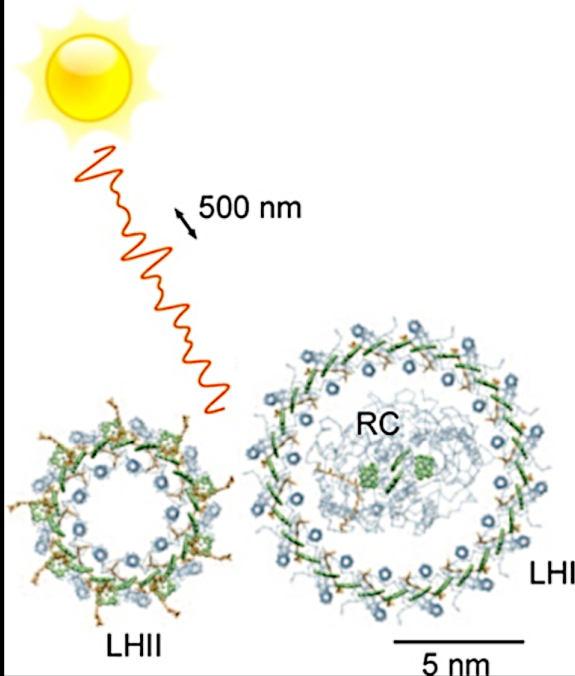
Unidirectional
transfer
(outer to inner wall)

Transfer from outer
wall to dark states

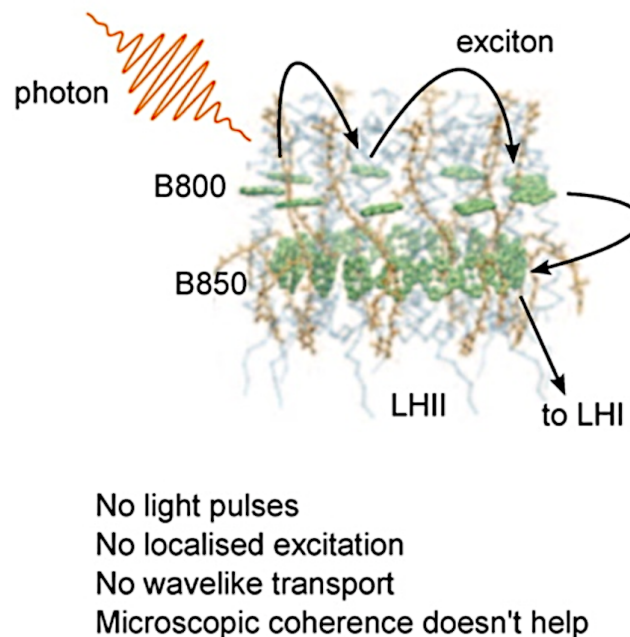
Sunlight vs a laser

NO TEMPORAL SUPERPOSITION IN PHOTOSYNTHESIS

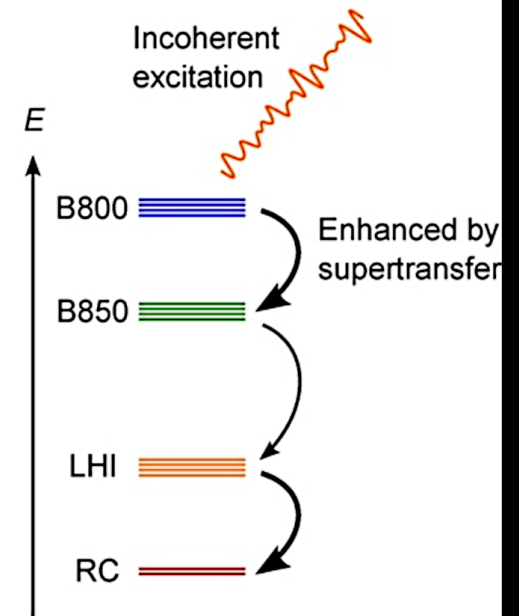
a. Sunlight: incoherent, stationary



b. An inaccurate picture:



c. A more accurate picture:



Ivan Kassal, J. Yuen-Zhou, and S. Rahimi-Keshari,
J. Phys. Chem. Lett. 4, 362 (2013)

Summary and additional questions

ABOUT COHERENT ENERGY TRANSFER

Designed first quantum process tomography scheme for chemistry: **approach to designing and obtaining information from ultrafast experiments**

Found previously elusive long-lived temporal quantum coherence in double-walled J-aggregate.



How does spatial coherent energy transfer manifest itself in biological systems?

Can spatial coherent transfer play a role in technology?



GREEN SULFUR BACTERIA
Chlorobaculum tepidum

10^{-4} W/m^2

300 near – IR photons/s

1 duplication / 3 – 26 years

250,000 BChl / antenna complex

~1 antenna complex / reaction center



SAGUARO
Carnegiea gigantea

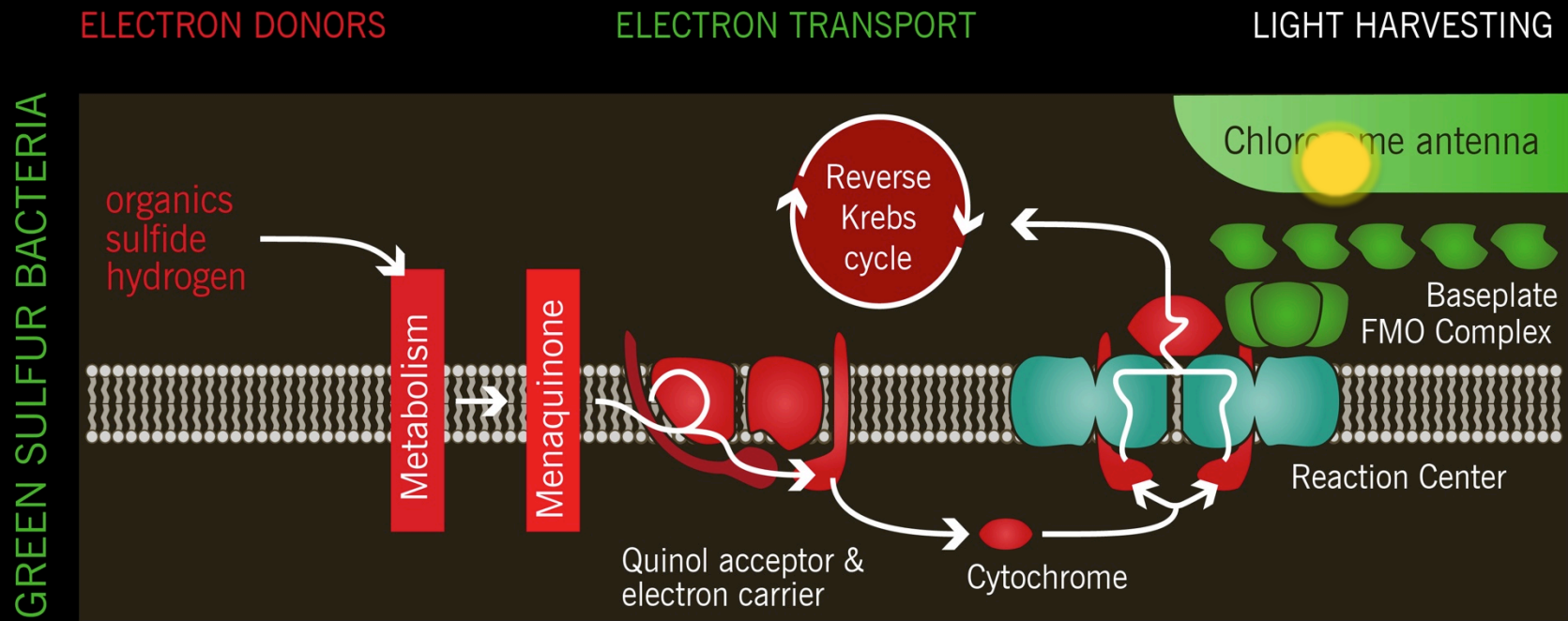
10^3 W/m^2

200 Chl / reaction center



Green-Sulfur bacteria

*Chlorobaculum tepidum**

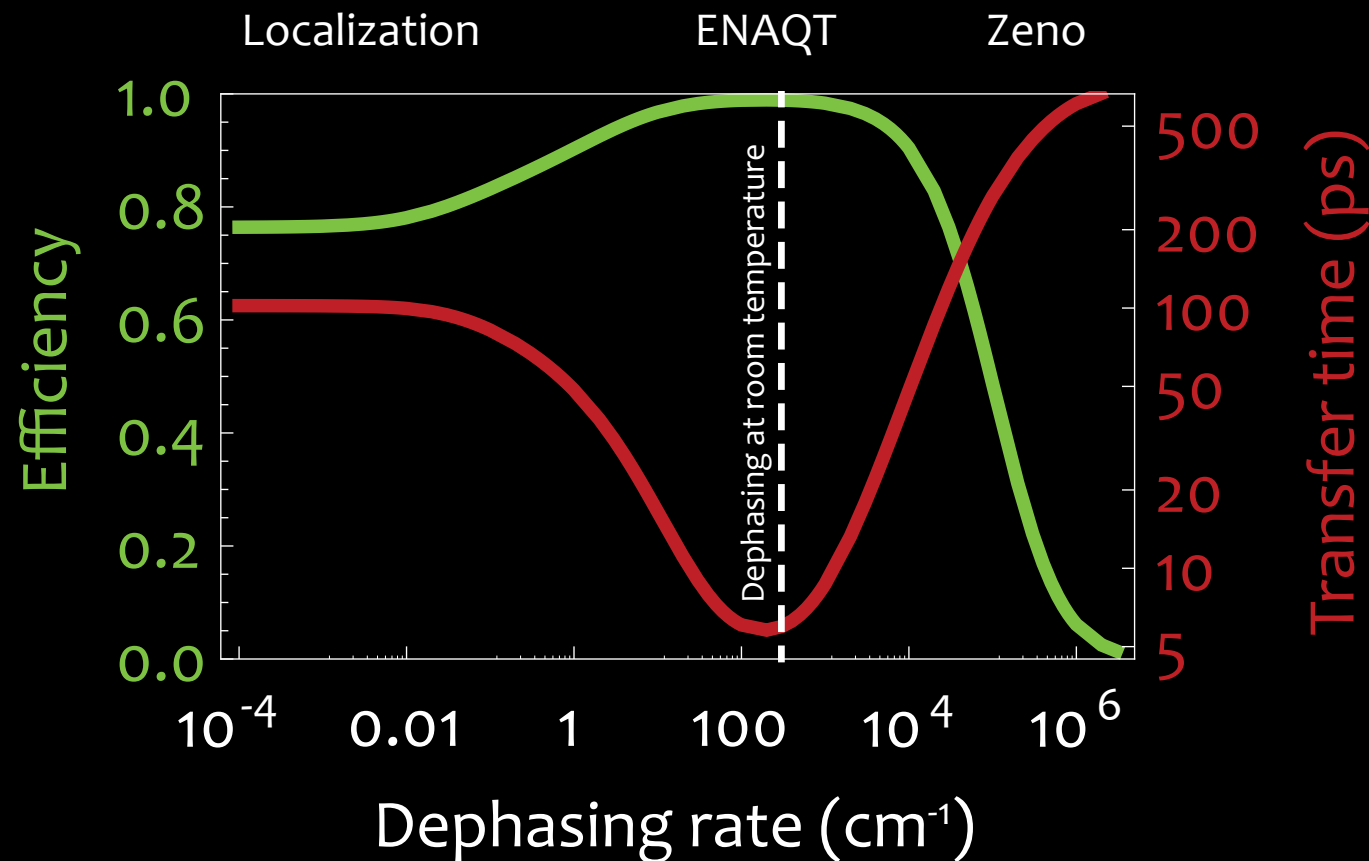


* aka *Chlorobium tepidum*

Image adapted from: M. F. Hohmann-Marriott and R. E. Blankenship, Ann. Rev. Plant. Biol. 211, 62 515 (2011)

Environment-Assisted Quantum Transport

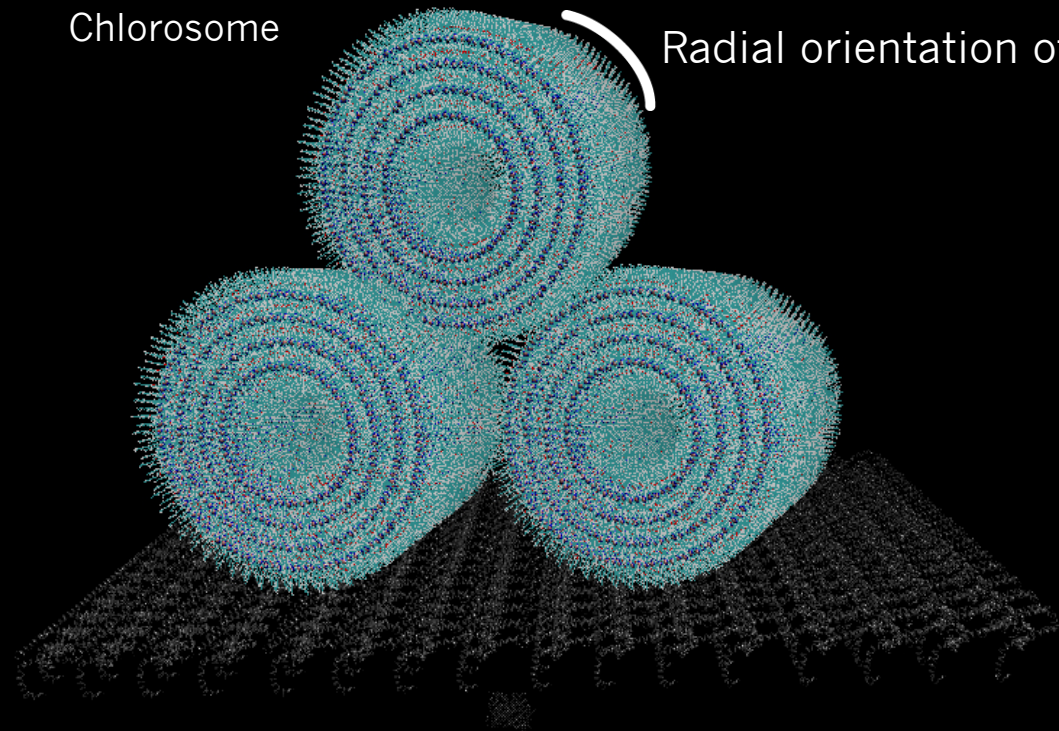
INTERPLAY OF QUANTUM AND CLASSICAL REGIMES



Where are we going **now**?

SYSTEMS-LEVEL ANALYSIS

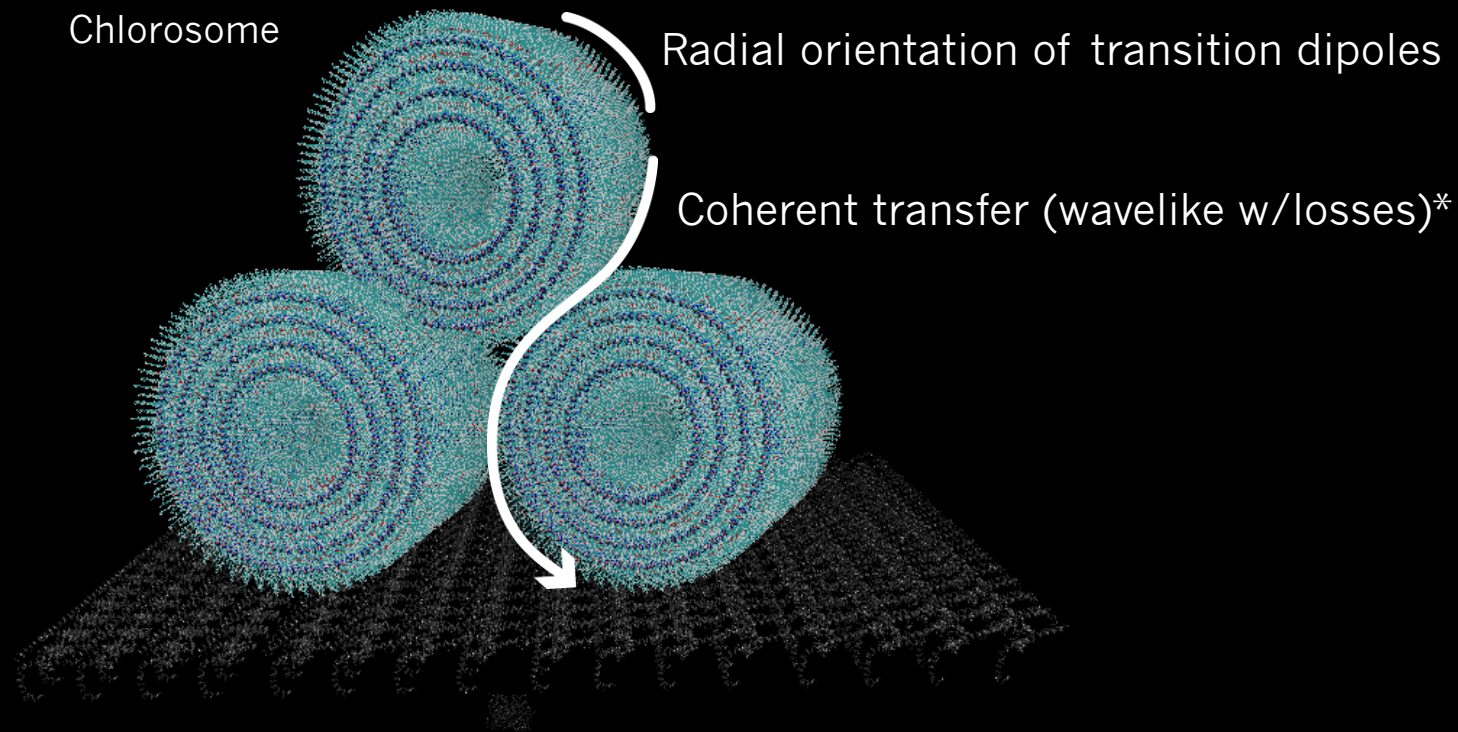
Chlorosome



Radial orientation of transition dipoles

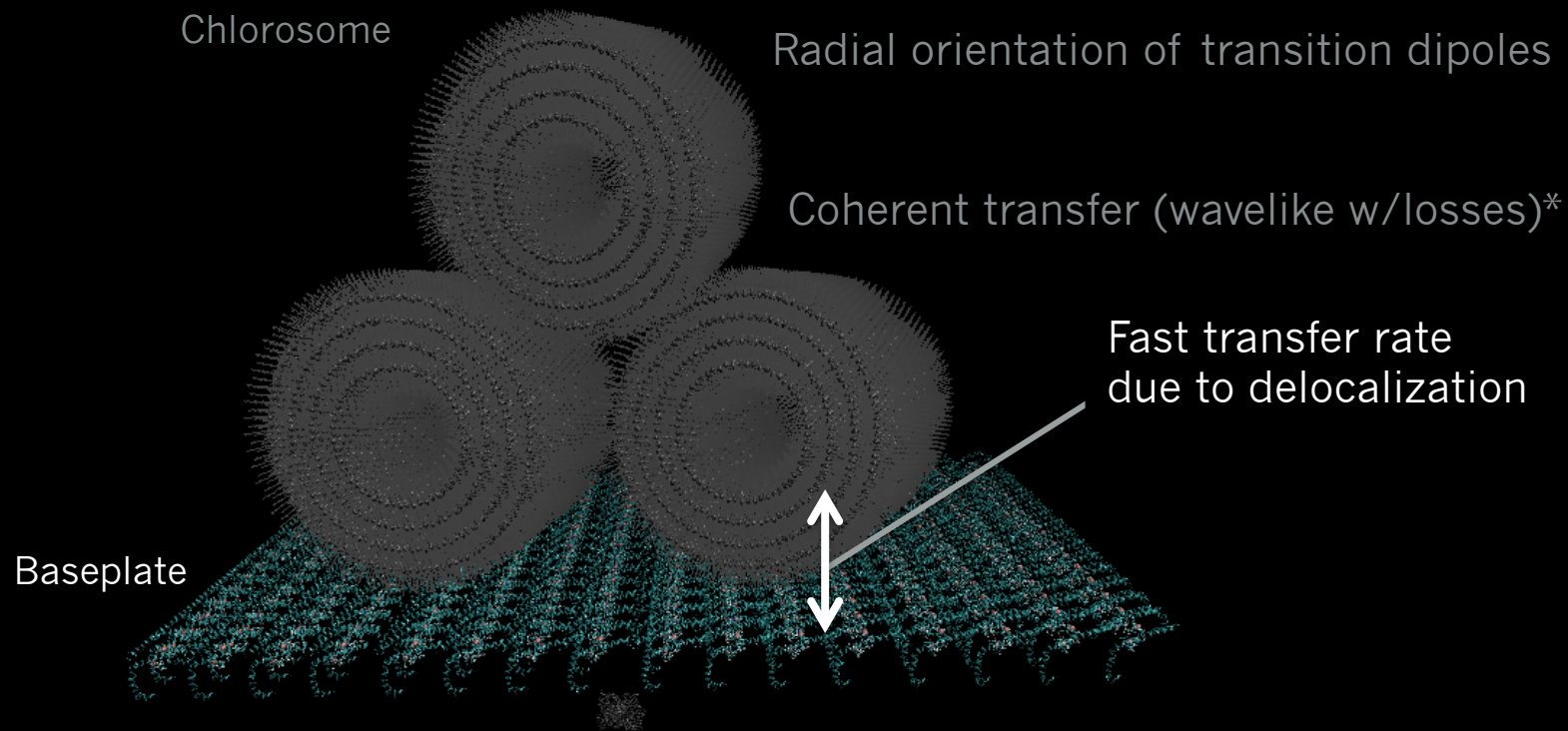
Where are we going **now**?

SYSTEMS-LEVEL ANALYSIS



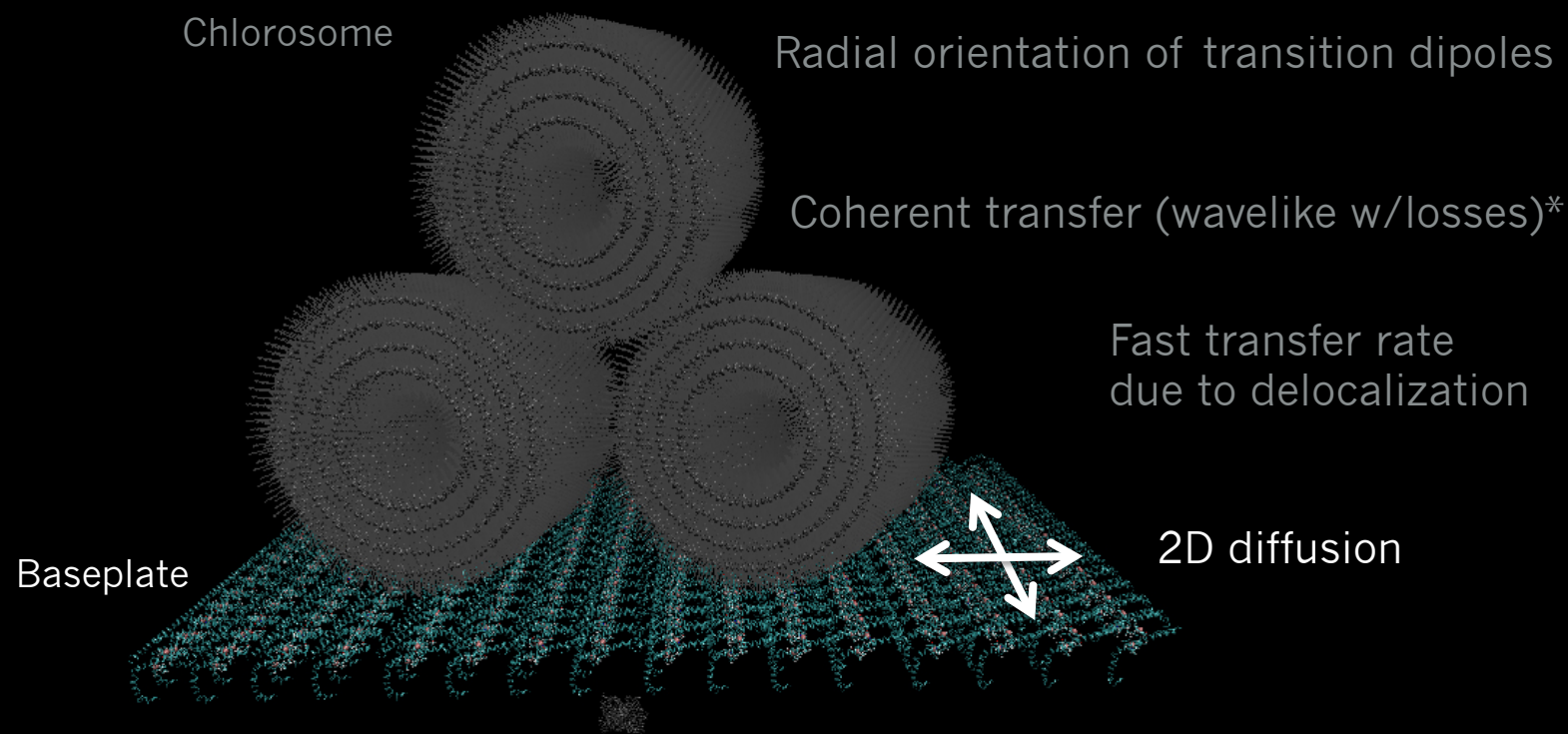
Where are we going **now**?

SYSTEMS-LEVEL ANALYSIS



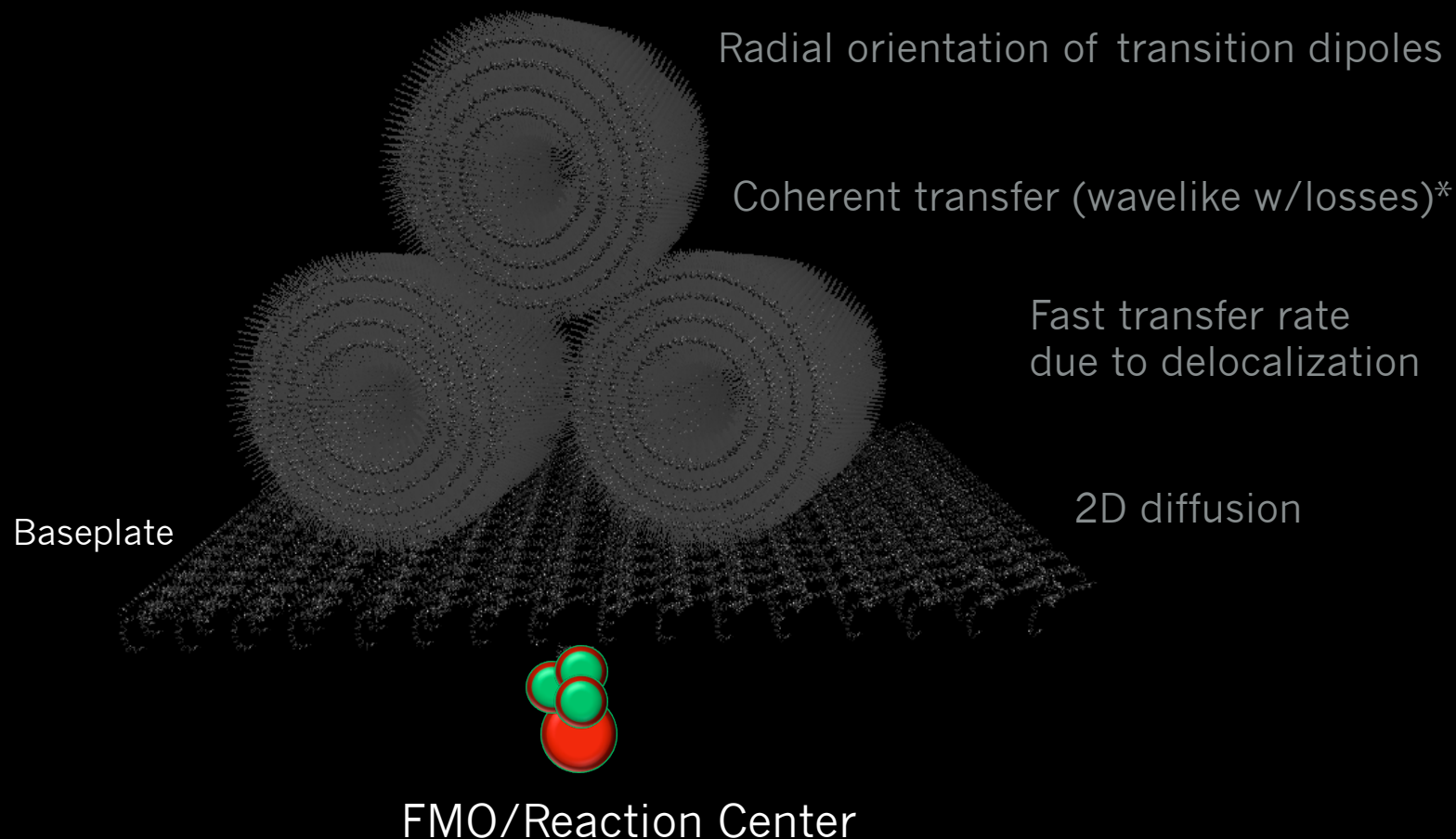
Where are we going **now**?

SYSTEMS-LEVEL ANALYSIS

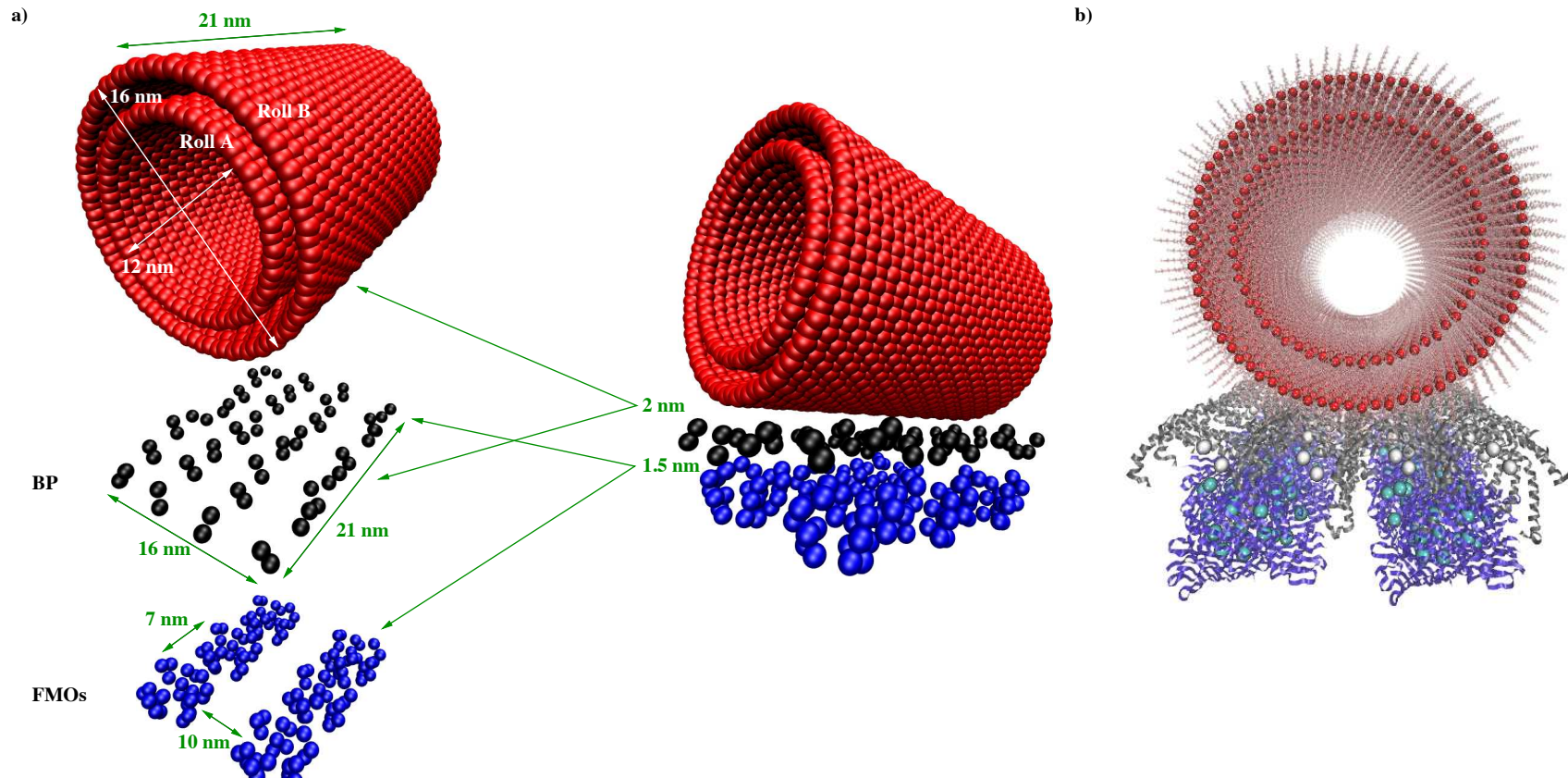


Where are we going **now**?

SYSTEMS-LEVEL ANALYSIS



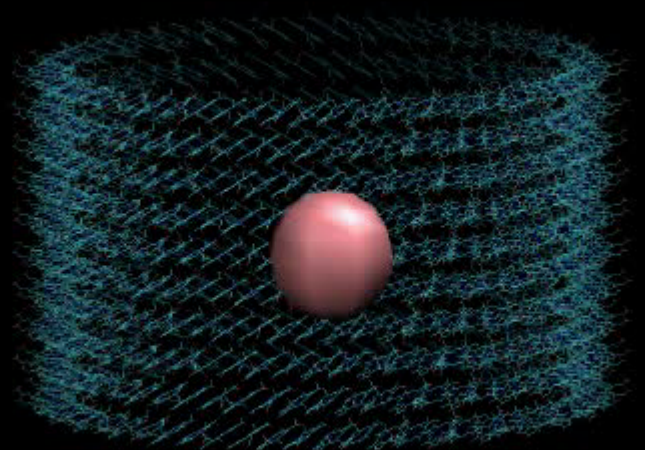
Atomistic model OF GREEN-SULFUR BACTERIA LIGHT-HARVESTING



J. Huh, J. Brookes, S. Saikin, S. Valleau, M. H. Yung, and A. Aspuru-Guzik, In Preparation (2013)

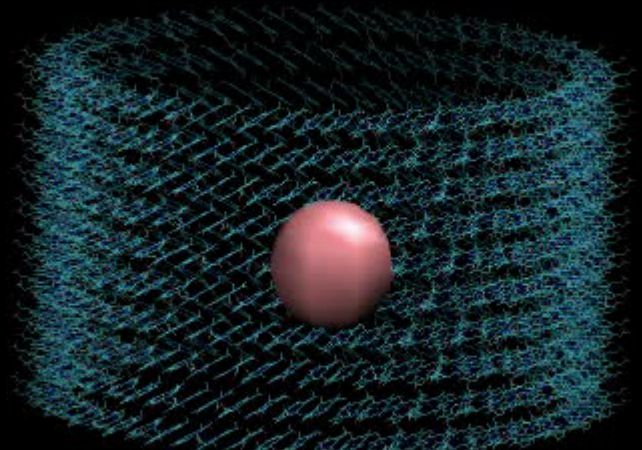
Exciton dynamics in the chlorosome

TIMESCALES



0.0 fs

Single-trajectory



0.0 fs

Ensemble

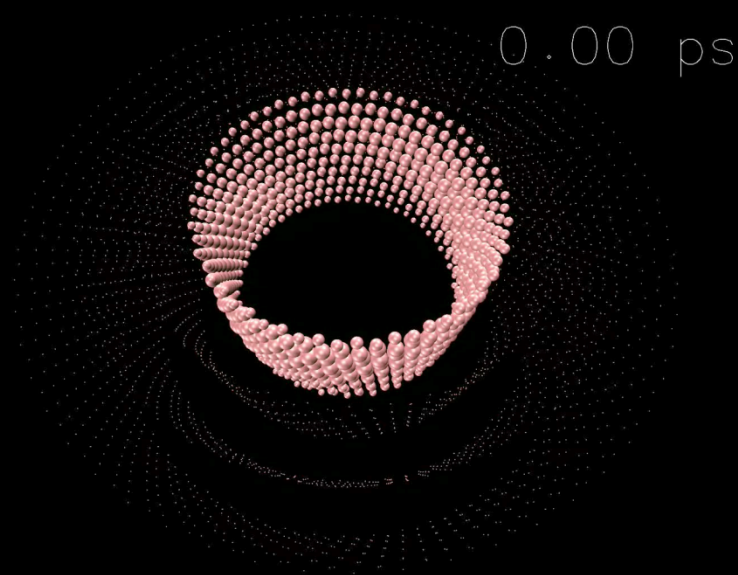
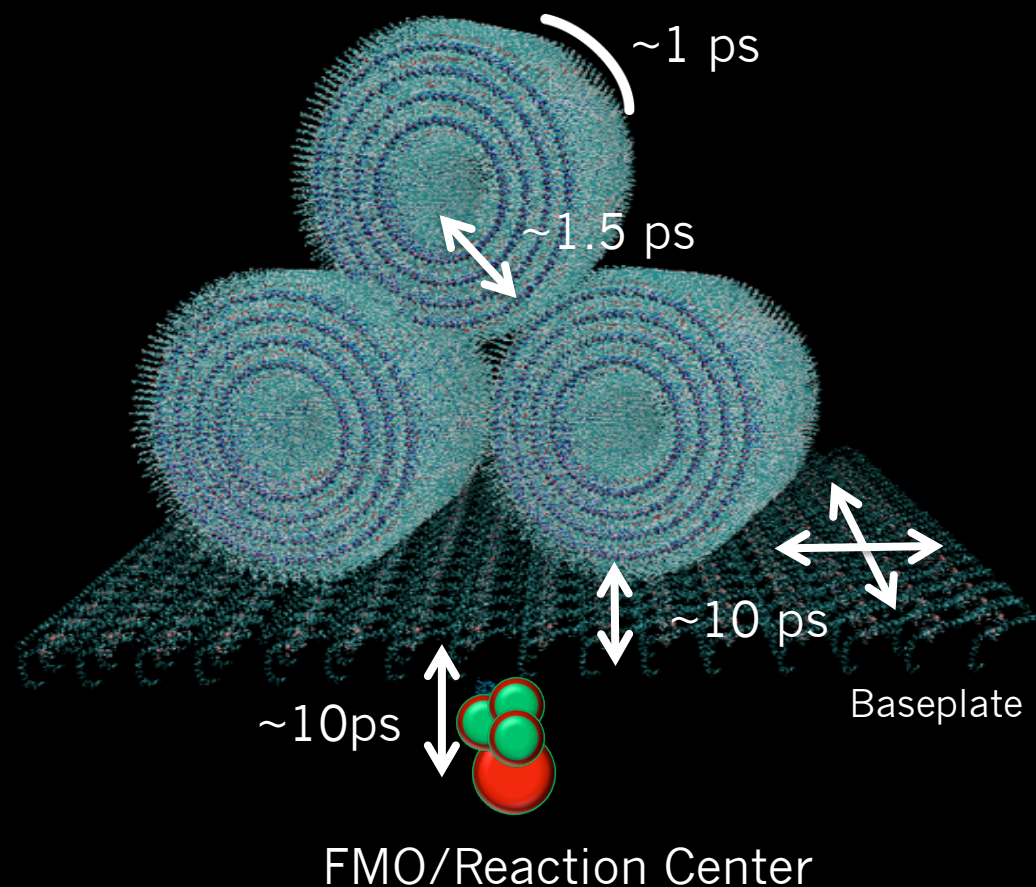
Theory: T. Fujita, J. C. Brookes, S. Saikin and A. Aspuru-Guzik, J. Phys. Chem. Lett. 3, 2357 (2012).

Updated theoretical model: T. Fujita, J. Huh, and A. Aspuru-Guzik, In Preparation.

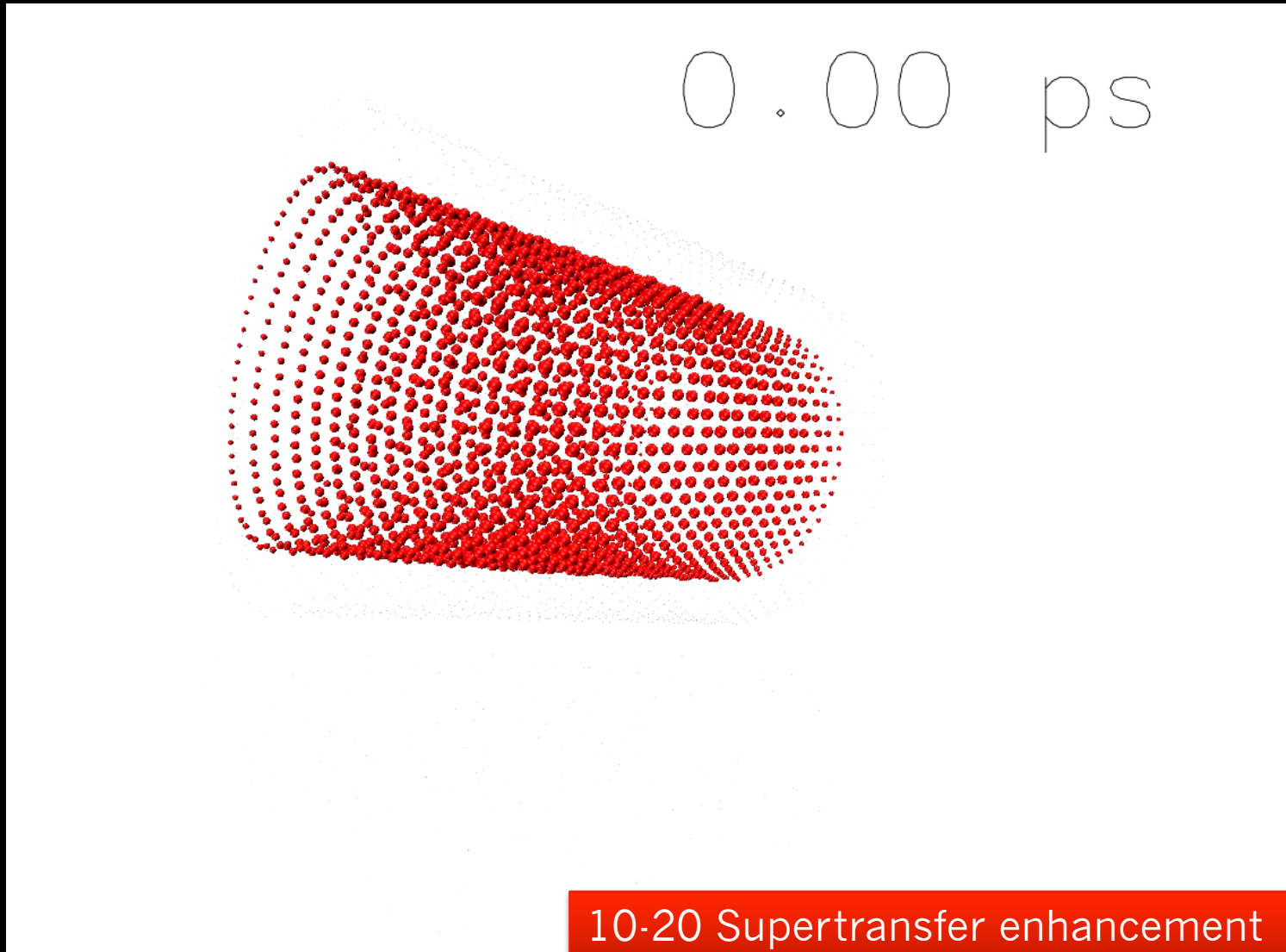
Experiment: D. Zigmantas, et al., J. Am. Chem. Soc. 134, 1161 (2012)

Chlorobium light-harvesting system

PREDICTED ENERGY TRANSFER TIMESCALES



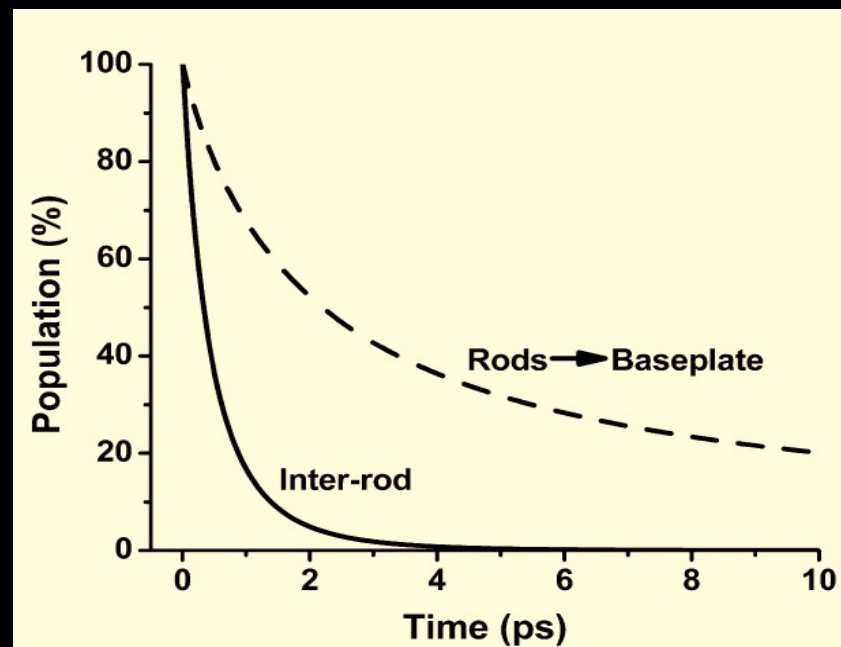
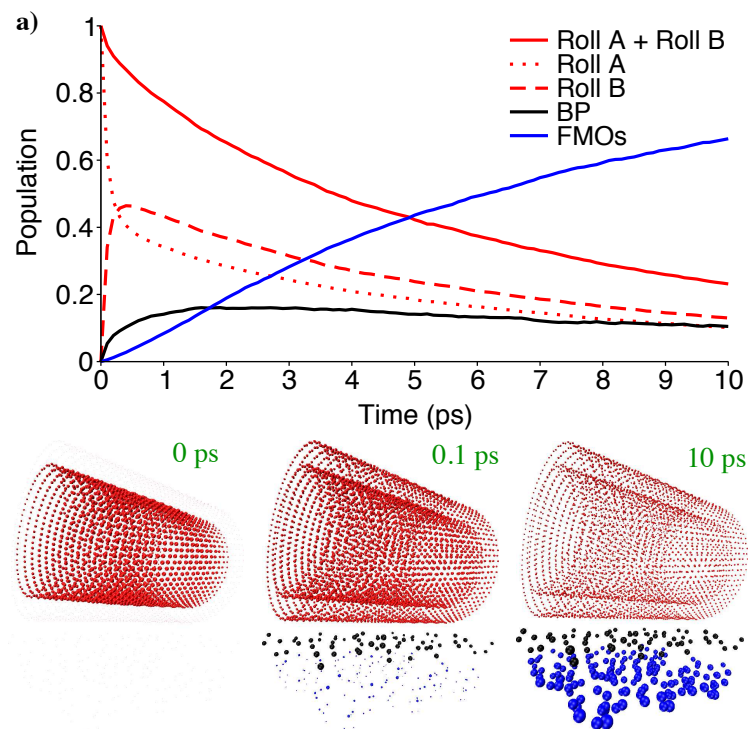
Chlorobium light-harvesting system



J. Huh, T. Fujita, J. Brookes, S. Saikin, S. Valleau, and A. Aspuru-Guzik, In Preparation (2013).

System-level energy transfer

PREDICTED ENERGY TRANSFER TIMESCALES



Exptl. roll-baseplate rate ~10 ps

Realistic FMO density model(6 FMO/300 nm²)

Theory: J. Huh, T. Fujita, J. Brookes, S. Saikin, S. Valleau, and A. Aspuru-Guzik, In Preparation.

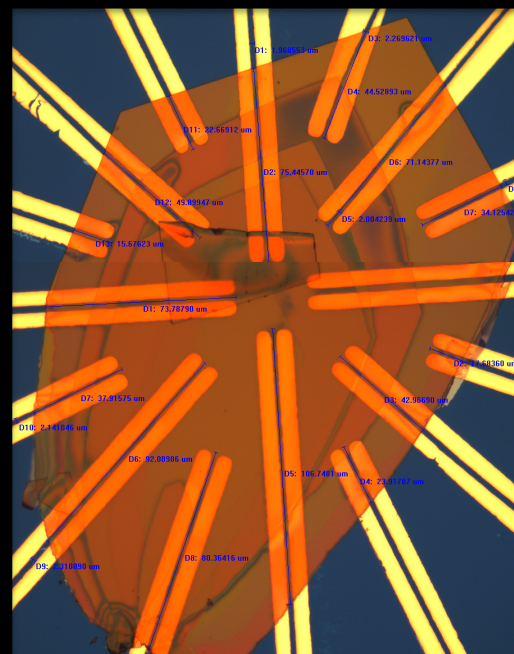
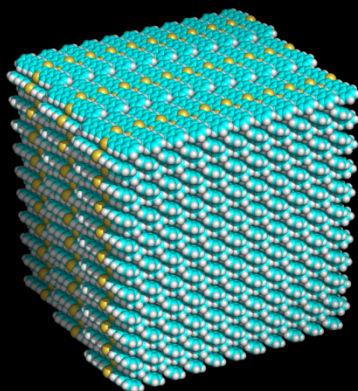
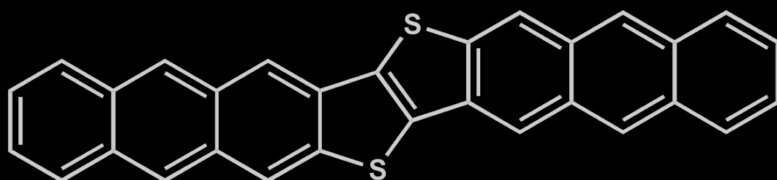
FMO density experiment: Wen, et al. Proc. Nat. Acad. Sci. 106 6134 (2009)

Absorption anisotropy decay experiment: Martiskainen, et al. Chem. Phys. Lett. 477 216 (2009)

Coherence in materials

TOWARDS LARGE HOLE-MOBILITY ORGANIC MATERIALS

Can coherent transfer play a role in technology?



DA2T crystal:
Hole mobility of $13 \text{ cm}^2/\text{Vs}$

Anatoly Sokolov, Sule Atahan-Evrenk, ..., Zhenan Bao, and Alán Aspuru-Guzik, Nat. Comm. 2, 437 (2011)
G. Giri, ..., Alán Aspuru-Guzik, Michael Toney, and Zhenan Bao, Nature 480, 504 (2011)

Coherence matters



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Thank you!

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