The Quantum Design of Photosynthesis

Rienk van Grondelle

KONINKLIJKE NEDERLANDSE AKADEMIE VAN WETENSCHAPPEN
130 jaar VU
PAPETS
NWO Nederlandse Organisatie voor Wetenschappelijk Onderzoek
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ICRA INSTITUT CANADIEN DE RECHERCHES AVANCÉES
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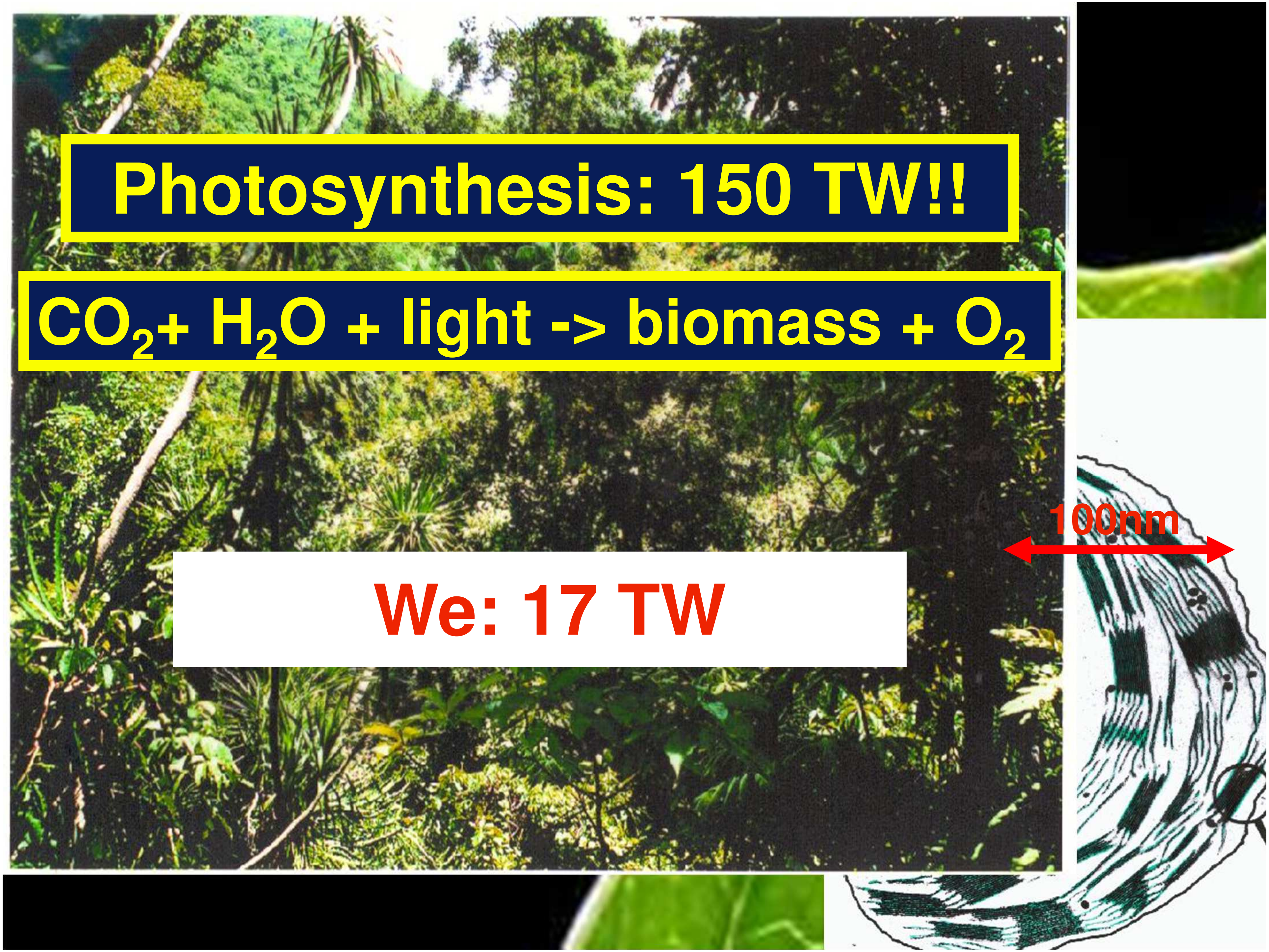
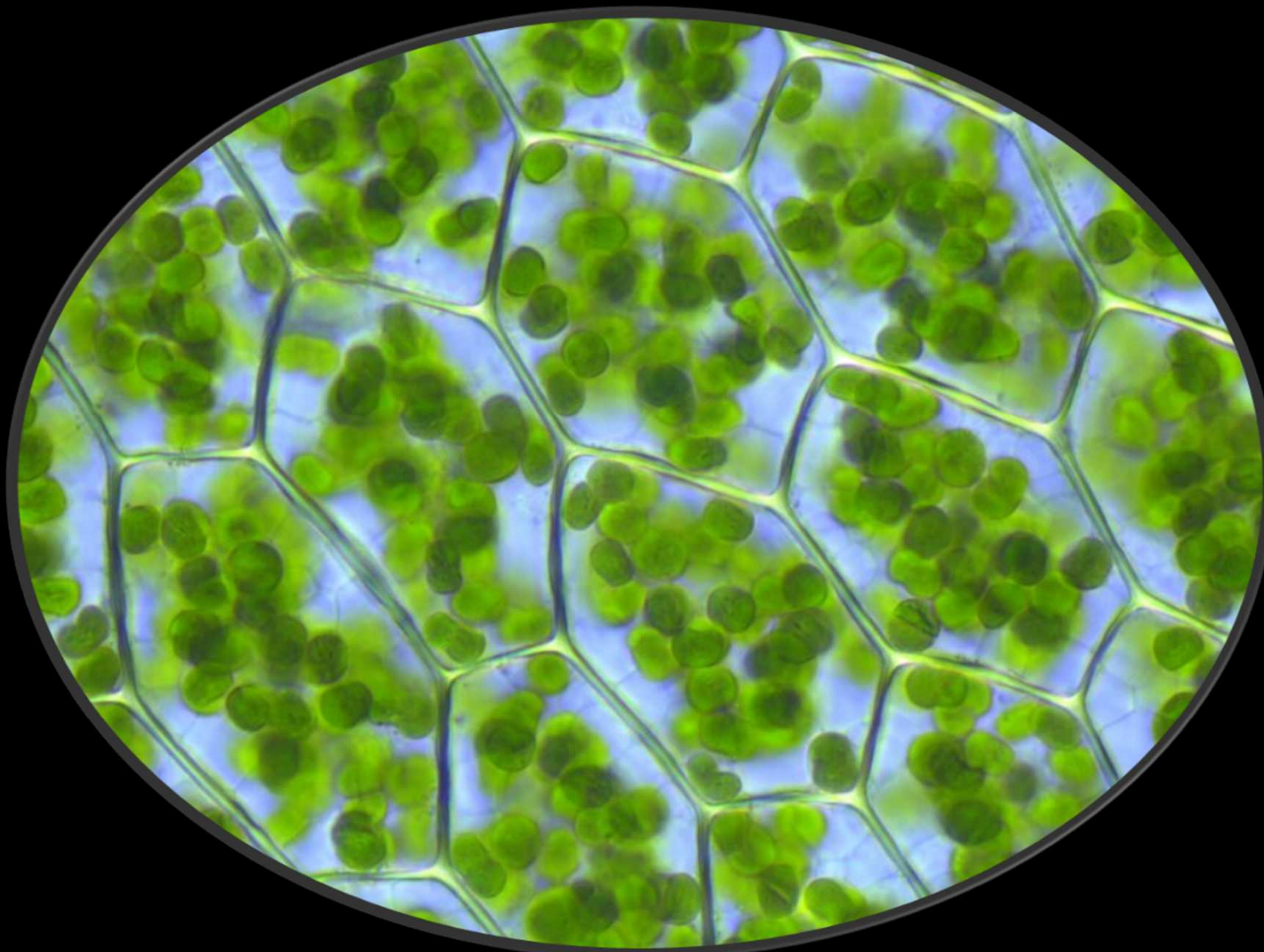

Photosynthesis: 150 TW!!
CO_2+ H_2O + light -> biomass + O_2
We: 17 TW
100nm

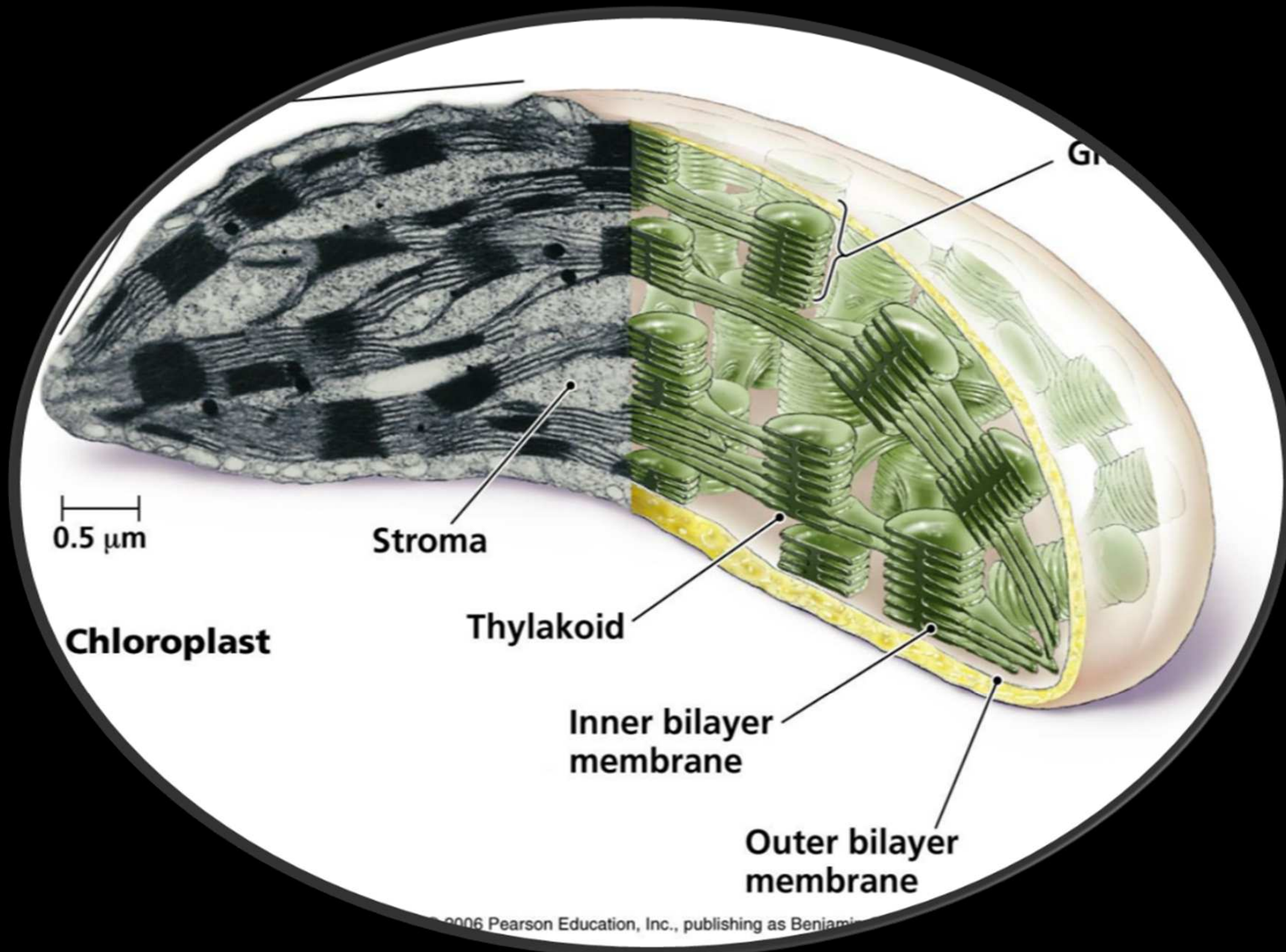
Photosynthetic Energy Conversion
in higher plants

Photosynthetic Energy Conversion

in higher plants

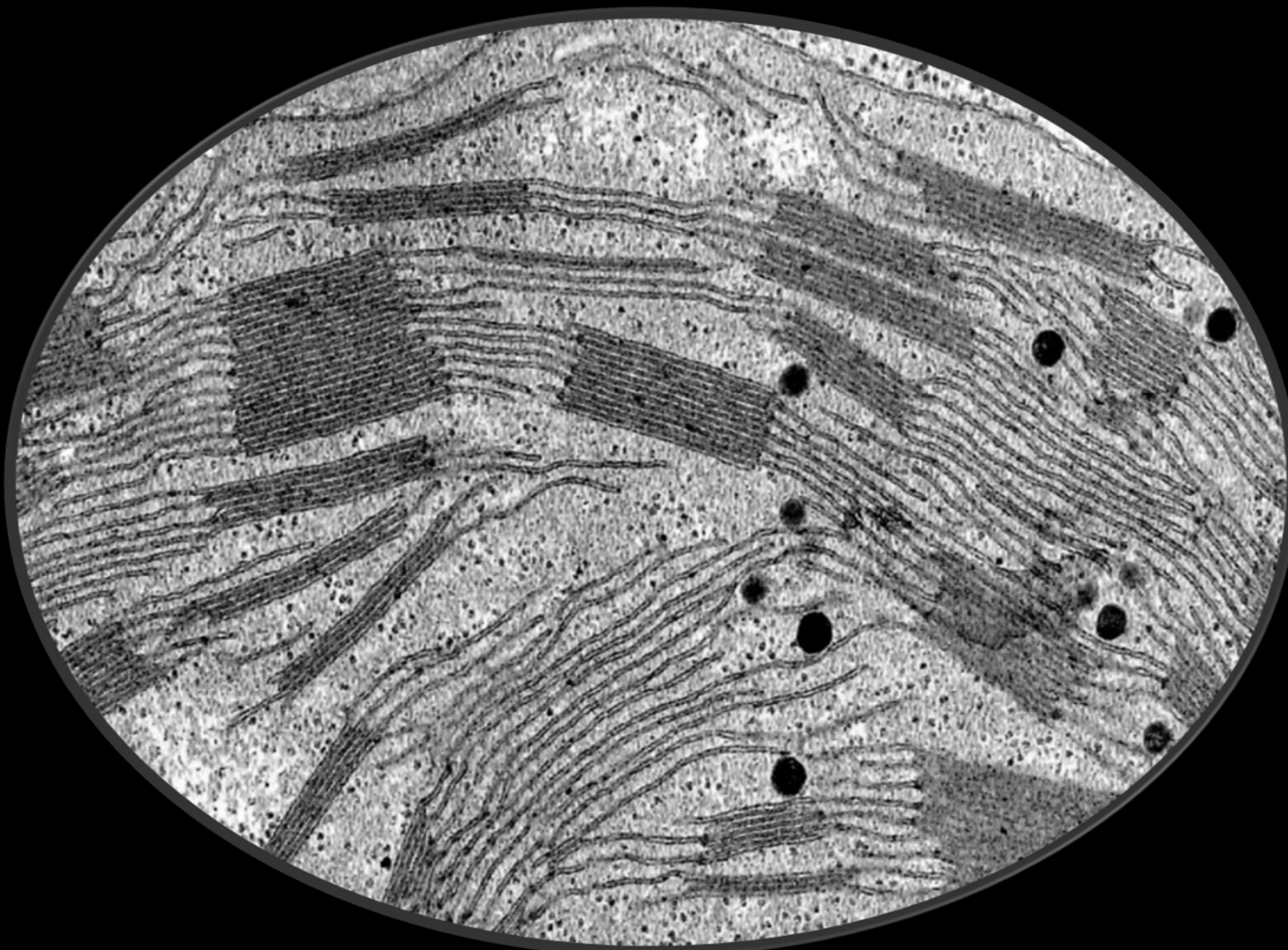


Photosynthetic Energy Conversion
in higher plants



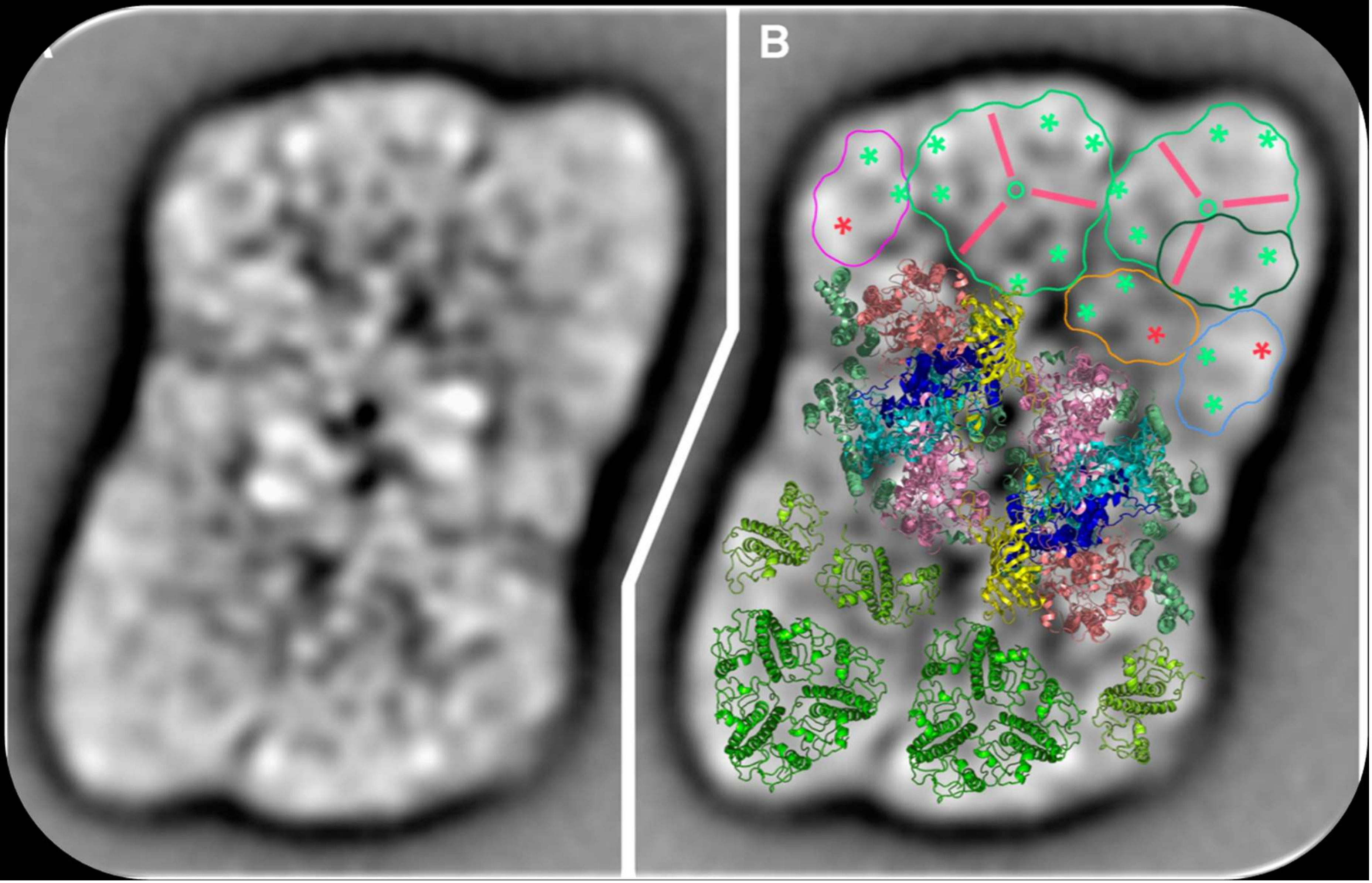
Photosynthetic Energy Conversion

in higher plants



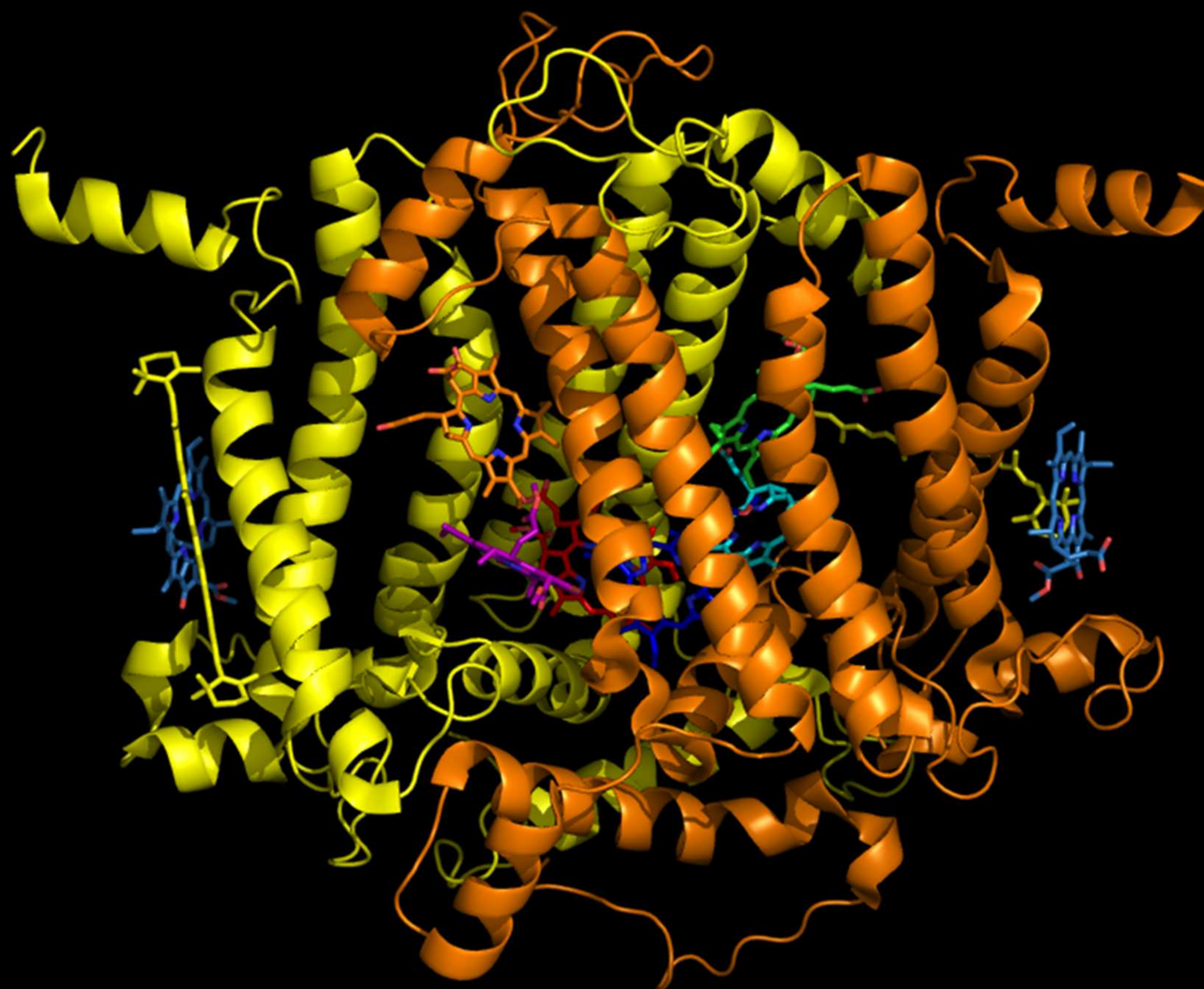
Photosynthetic Energy Conversion

in higher plants



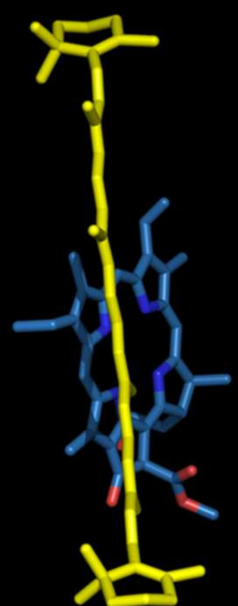
Photosynthetic Energy Conversion

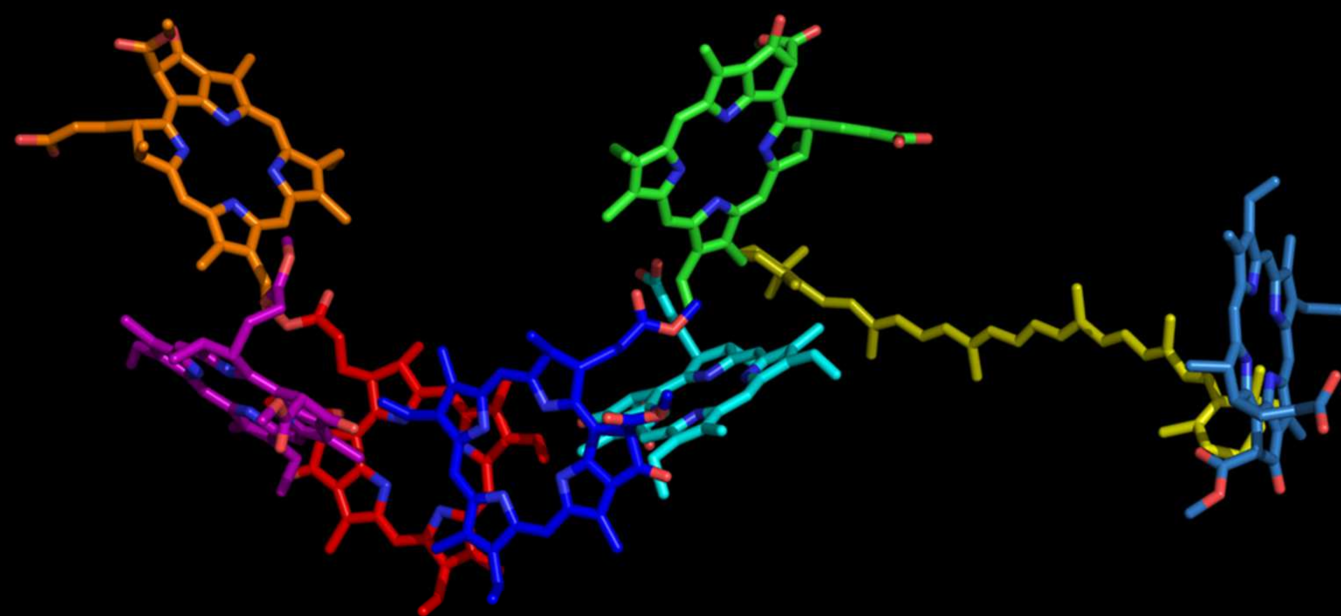
in higher plants



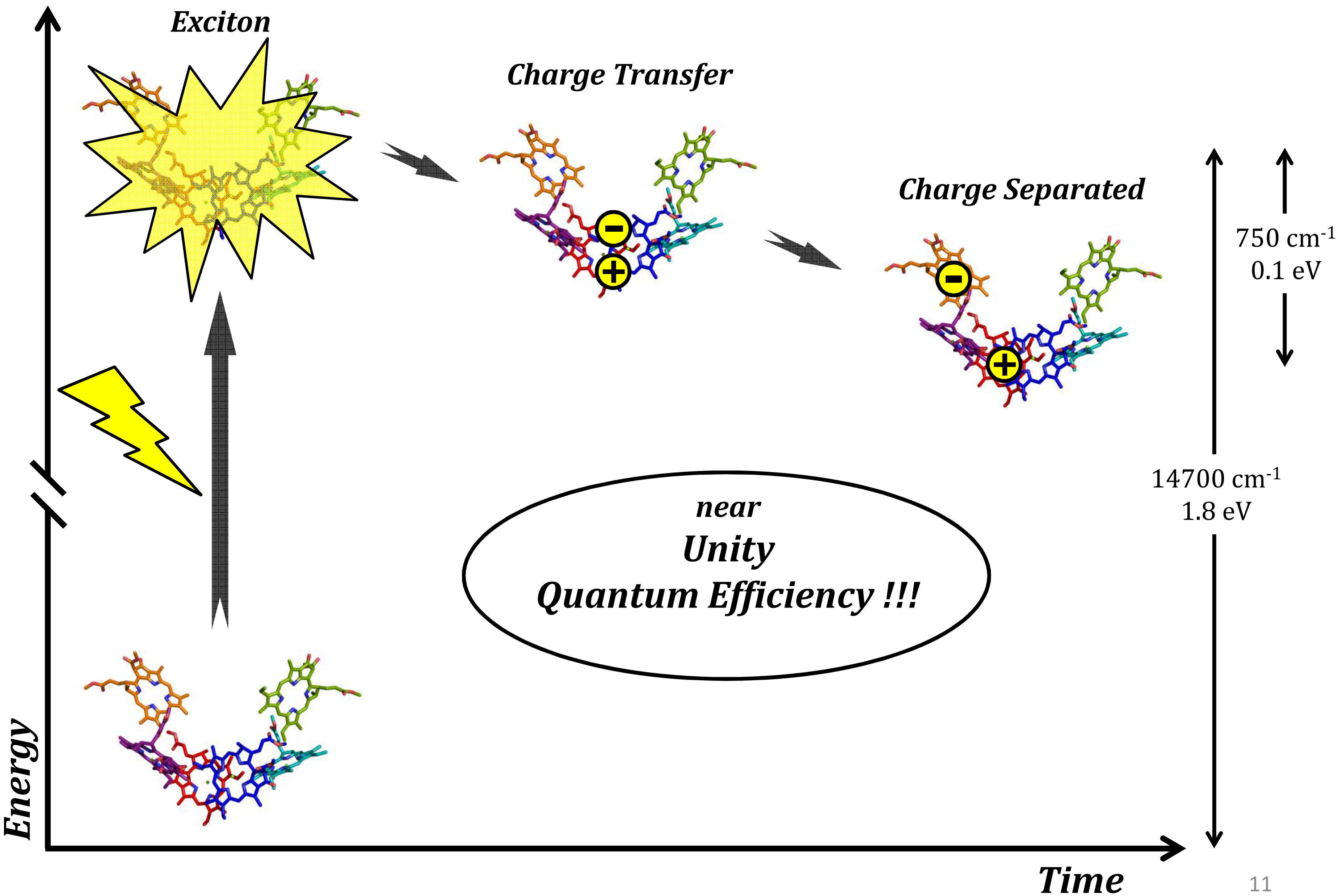
Photosynthetic Energy Conversion

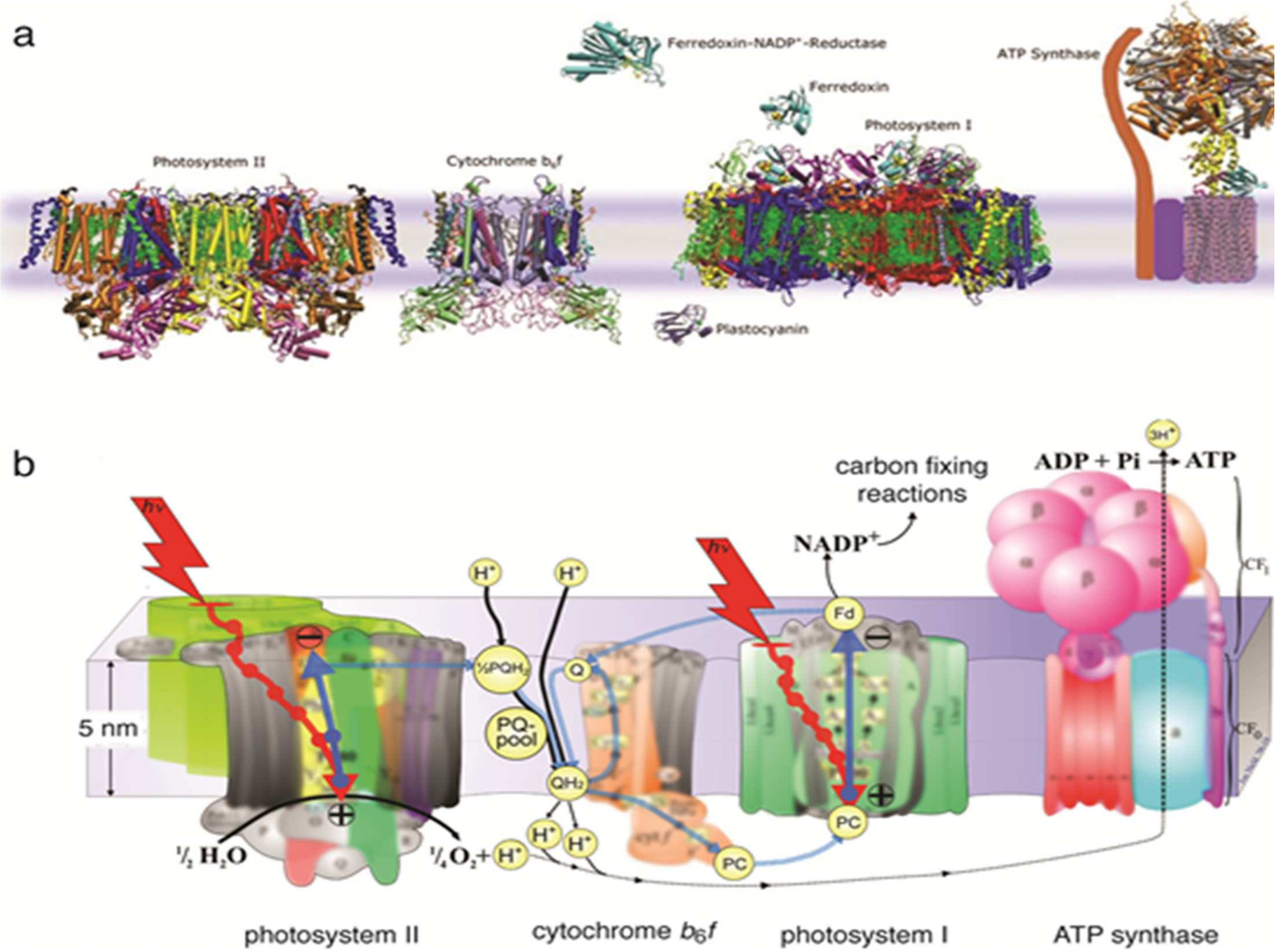
in higher plants





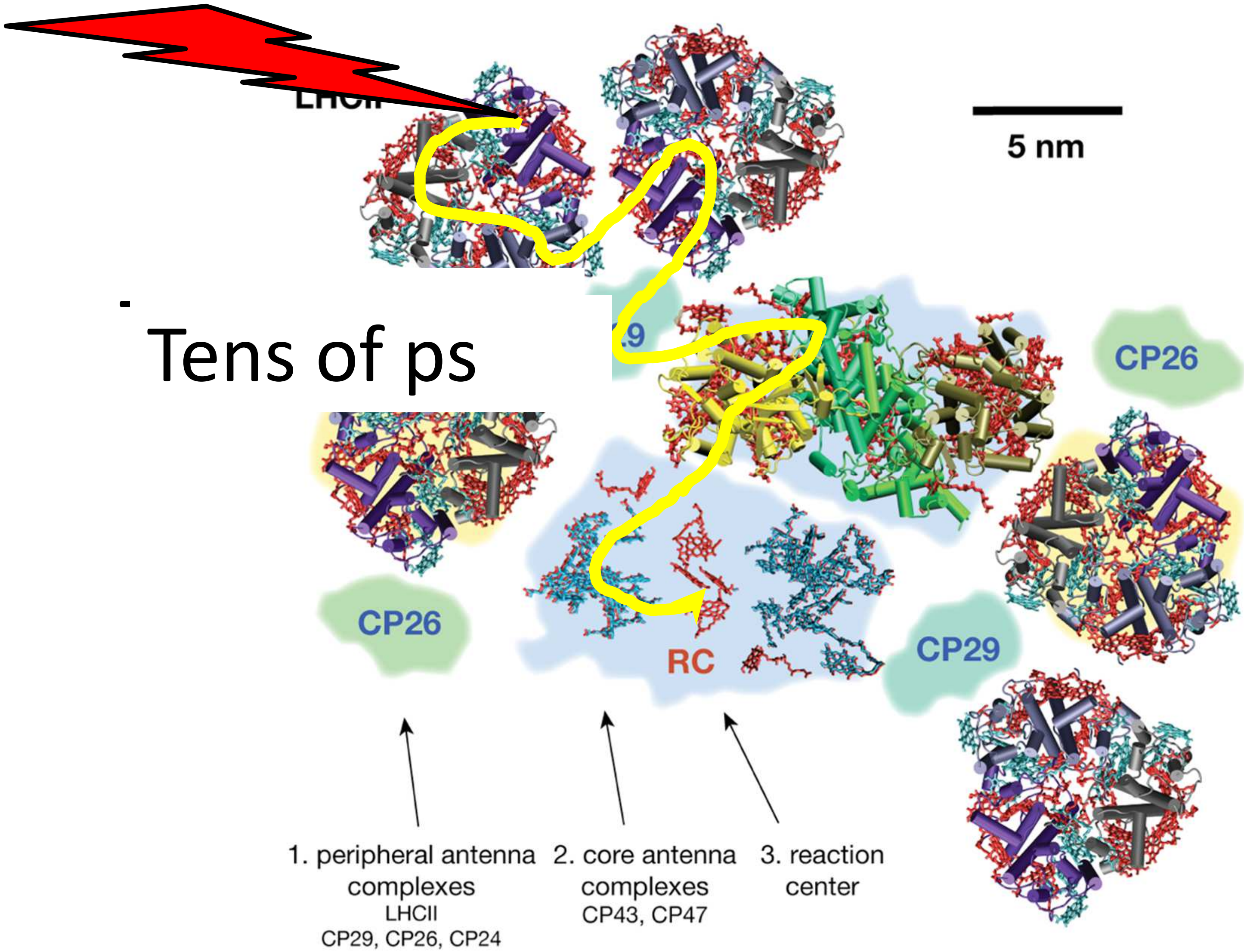
Charge Separation

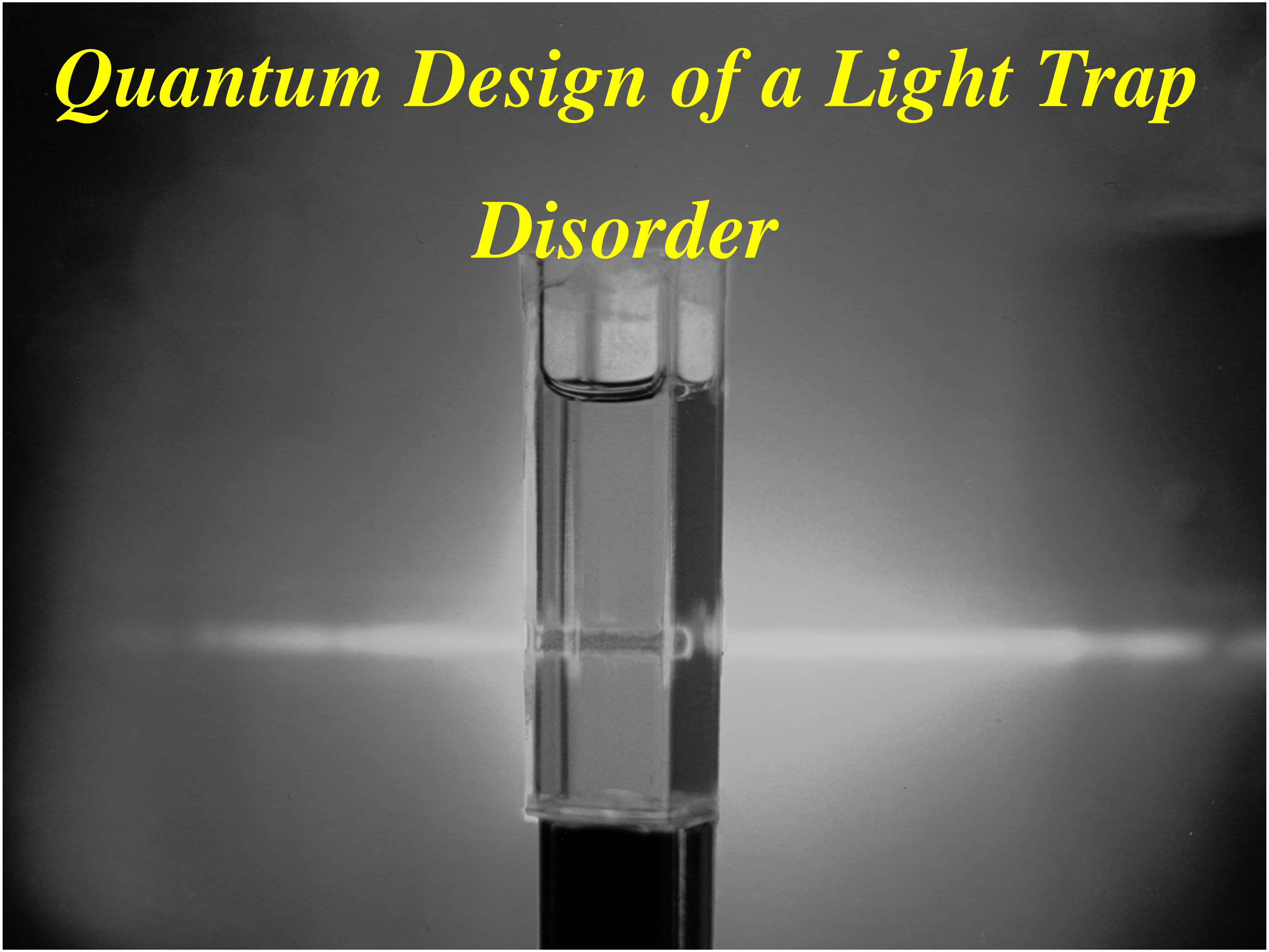



a
Ferredoxin-NADP⁺-Reductase
Ferredoxin
Photosystem I
ATP Synthase
Photosystem II
Cytochrome b₆f
Plastocyanin
b
carbon fixing reactions
NADP⁺
ADP + Pi → ATP
3H⁺
hv
H⁺
½PQH₂
PQ-pool
Q
QH₂
Fd
PC
5 nm
½ H₂O
¼O₂+H⁺
CF₁
CF₀
photosystem II
cytochrome b₆f
photosystem I
ATP synthase

Light harvesting

concentrates electronic excitation–*ultrafast* & efficient

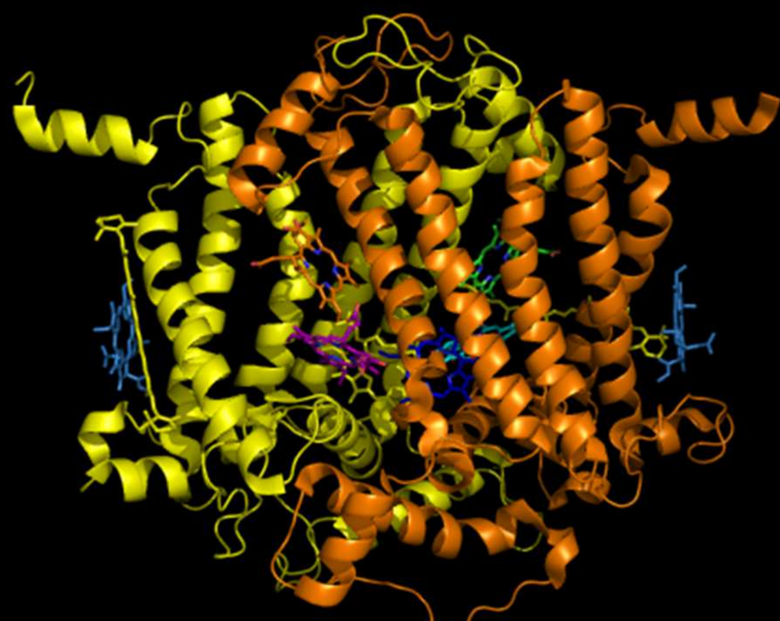



Quantum Design of a Light Trap
Disorder

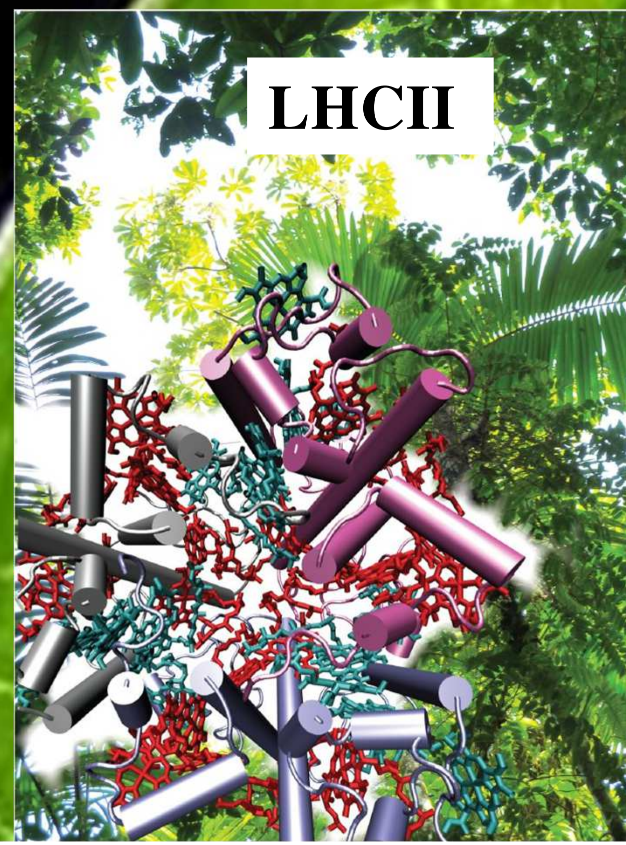
r19

In spite of the fact that Nature appears ordered there is disorder = Energetic Disorder

- Disorder in local environment
- Disorder in coupling (excitons, charge transfer, reorganization)
- All time scales: femtoseconds-seconds!!!



PSII Reaction Center



r19 Schematic view of how energy flows among the three subunits of the Lhc2 trimer, assuming one could excite Chla a 603(1) selectively (this is a computational result, the model is based on a multitude of experimental data). Top left: 603(1)* will EET mainly to the 610-611-612 cluster in the same subunit (< 1ps), a bit will transfer to 602(2), some to 602(1). The excited 610-611-612 trimer will relax mainly through uphill transfer to the lowest exciton state of 602-603(1), which is mainly 602(1). Since this is uphill it is slow. The most obvious energy acceptor for 602(1) is 603(3), which again is uphill and again is slow (slow here means 10-20 ps).
Right bottom. This figure tries to explain some of thos EET steps. Red is 602, magenta is 603. 603 is energetically above 602 meaning that in all the subunits of this pair the highest exciton state is determined by 603(magenta), the lowest by 602 (red). Exciting 603(1) involves relaxation to 602(1), all the other rates are very slow (this of course on top of relaxation to the 610-611-612 trimerof subunit 1 which is even faster). Excitation of 602(1), either directly by 603(1) or by the 610-611-612 trimer of subunit escapes mainly via uphill transfer to the 603(3) (the 16 ps arrow in the bottom figure)
van grondelle, 8/17/2010

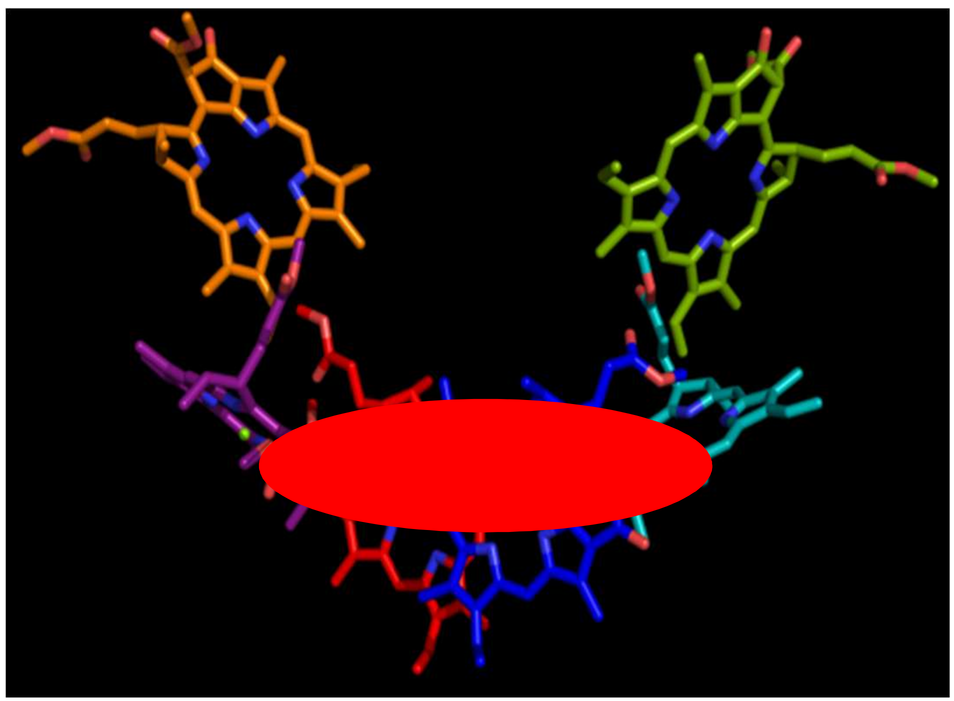
Quantum Design Principles of Photosynthesis

and Strategies to overcome Energetic Disorder

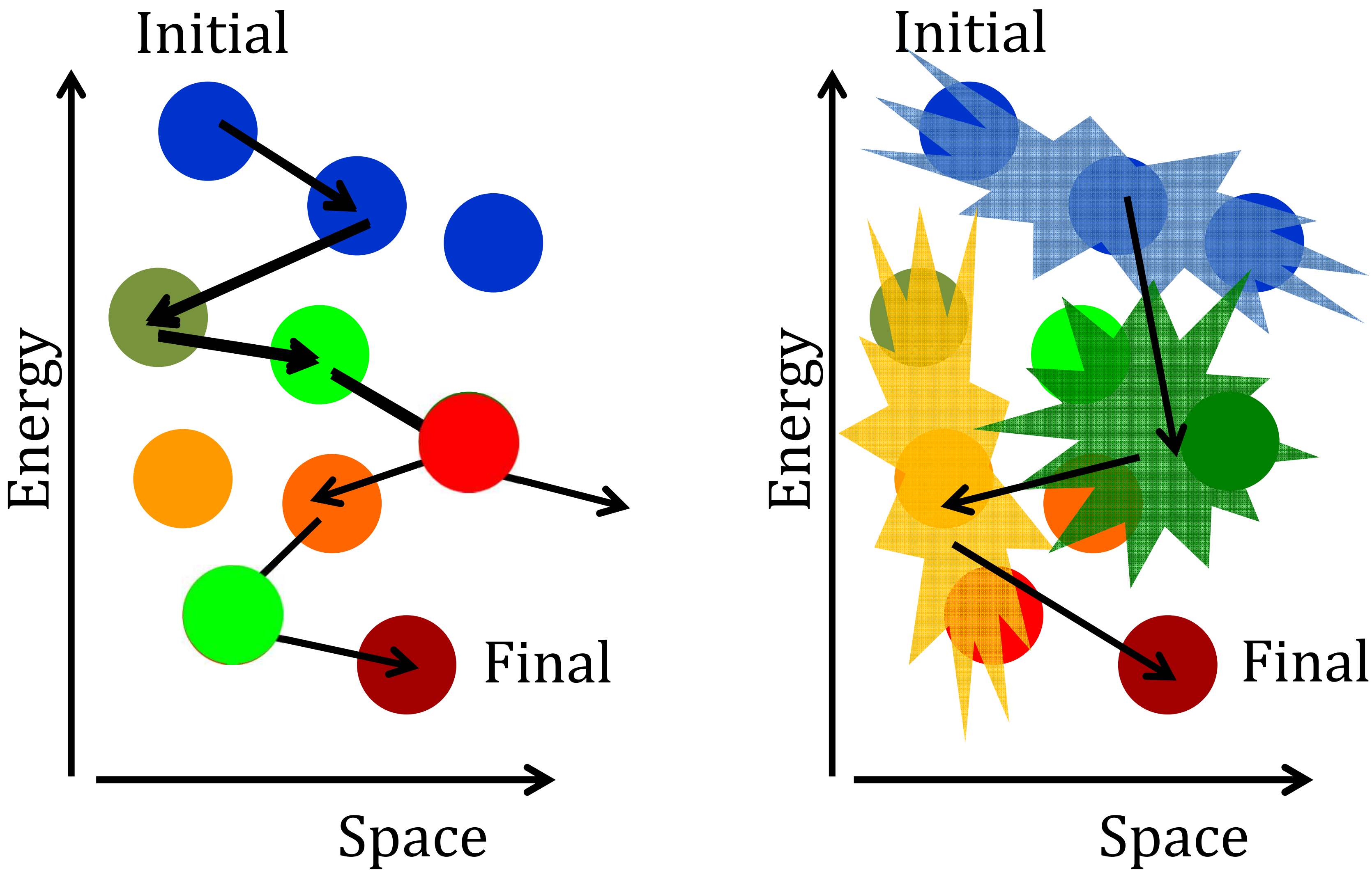
1st

Excitons
= Delocalized Excitations

$$\psi_k = \sum_{i=1}^{N} c_{ki}\varphi_i$$



Excitons

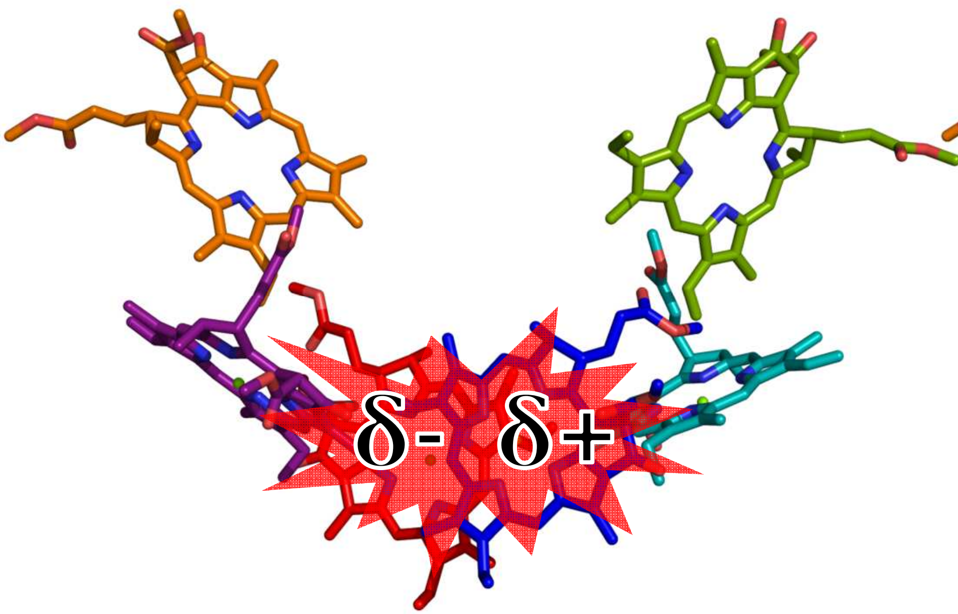


Individual pigments

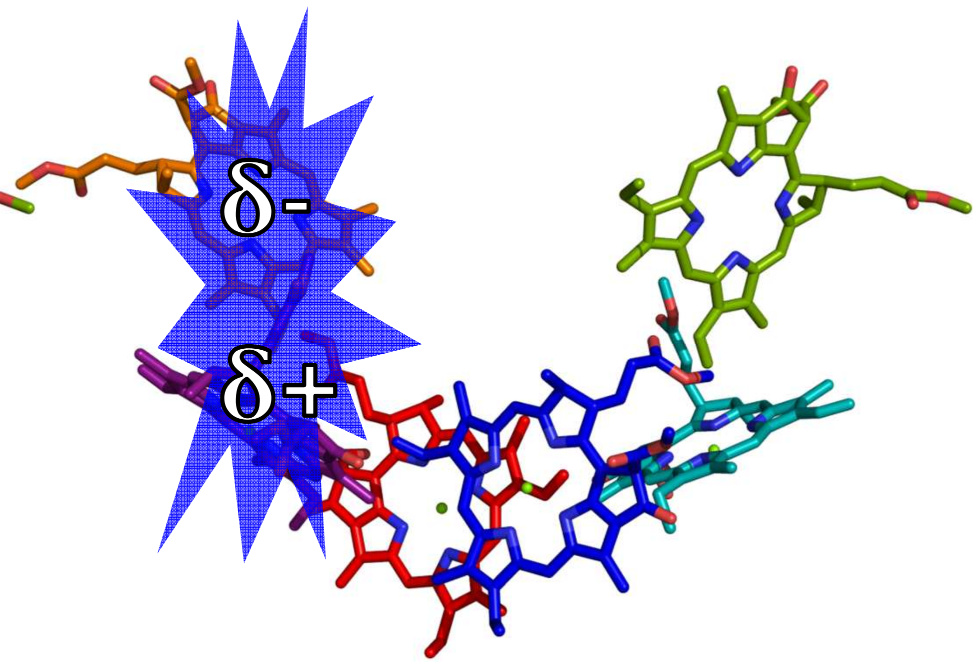
Excitons

2nd

Excitons with Charge-Transfer Character

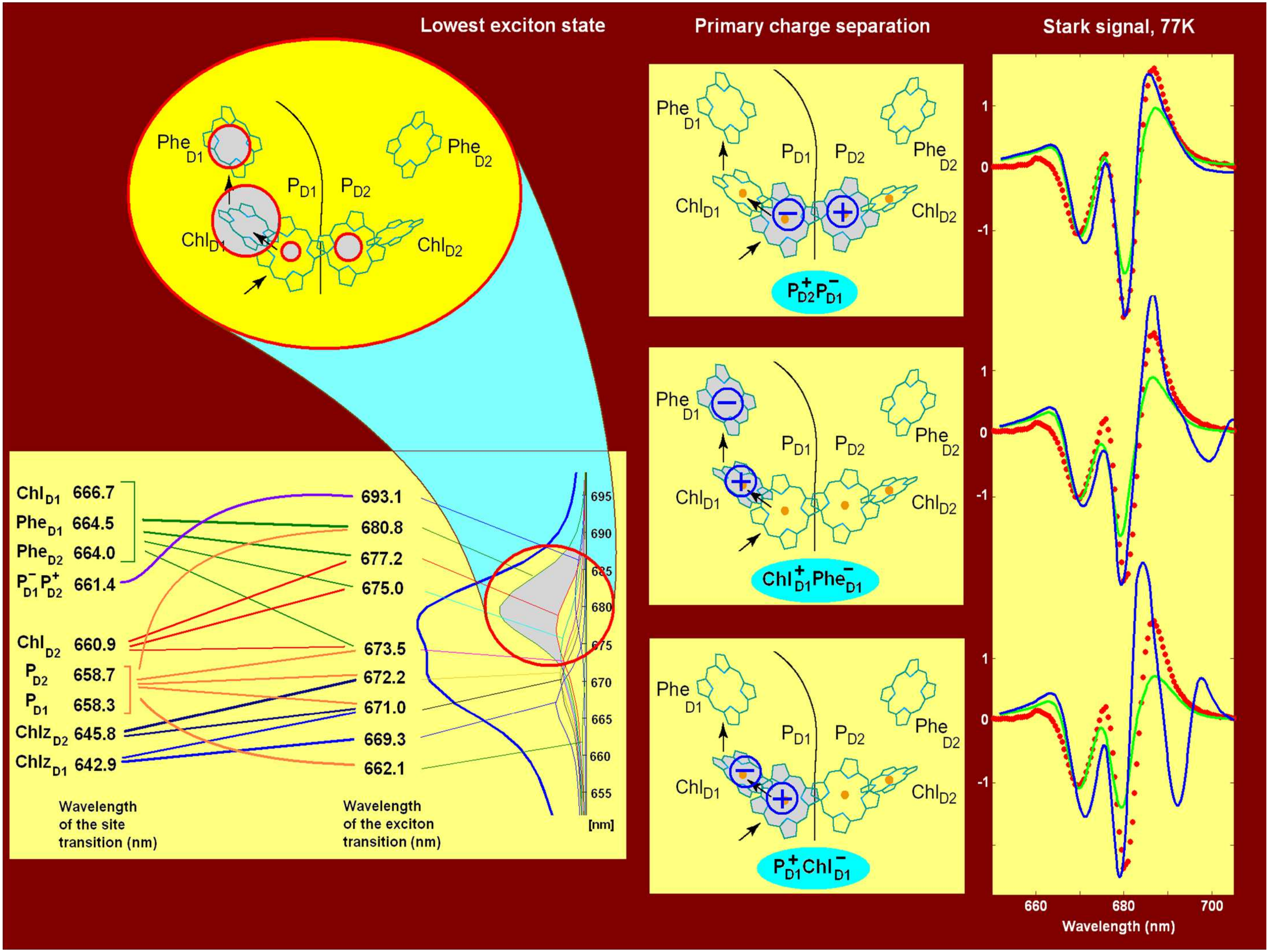


$P_{D2}^{\delta+} P_{D1}^{\delta-}$



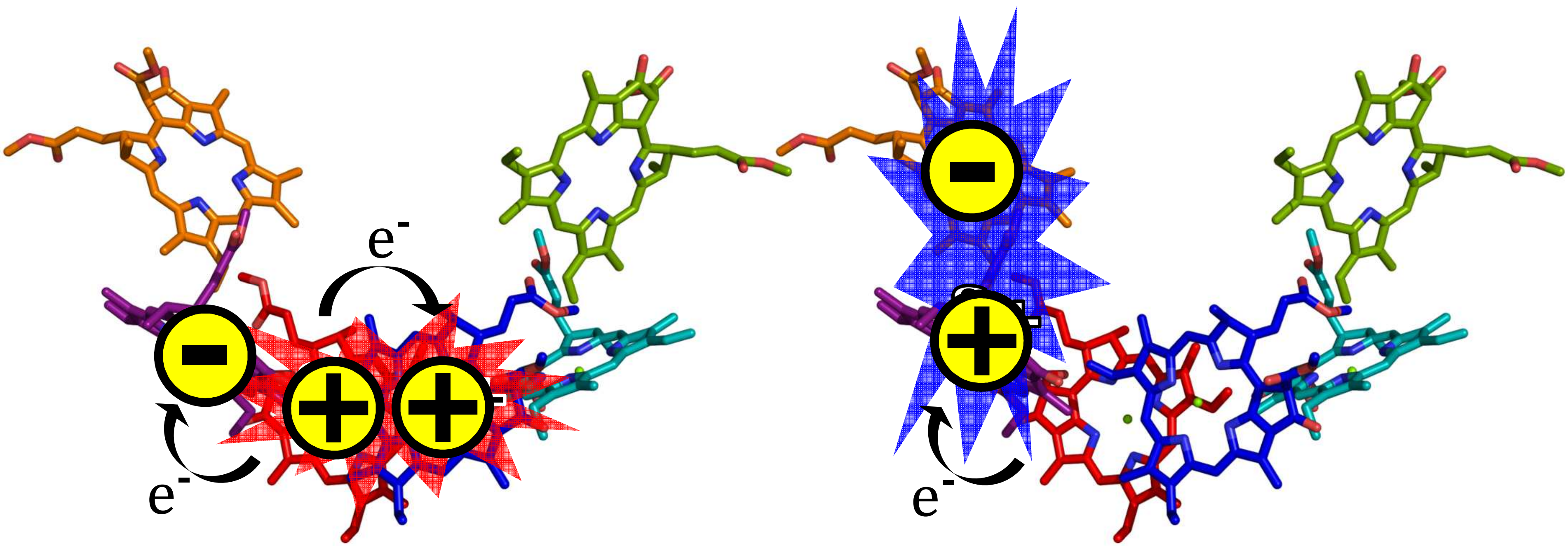
$Chl_{D1}^{\delta+} Phe_{D1}^{\delta-}$

Novoderezhkin et al, *Biophysical Journal*, **2007**
Romero et al, *Biophysical Journal*, **2012**



Lowest exciton state
Primary charge separation
Stark signal, 77K
Phe D1
Phe D2
P D1
P D2
Chl D1
Chl D2
$P^+_{D2}P^-_{D1}$
$Chl^+_{D1}Phe^-_{D1}$
$P^+_{D1}Chl^-_{D1}$
Chl_{D1} 666.7
Phe_{D1} 664.5
Phe_{D2} 664.0
$P^-_{D1}P^+_{D2}$ 661.4
Chl_{D2} 660.9
P_{D2} 658.7
P_{D1} 658.3
$Chlz_{D2}$ 645.8
$Chlz_{D1}$ 642.9
693.1
680.8
677.2
675.0
673.5
672.2
671.0
669.3
662.1
Wavelength of the site transition (nm)
Wavelength of the exciton transition (nm)
695
690
685
680
675
670
665
660
655
[nm]
1
0
-1
660
680
700
Wavelength (nm)

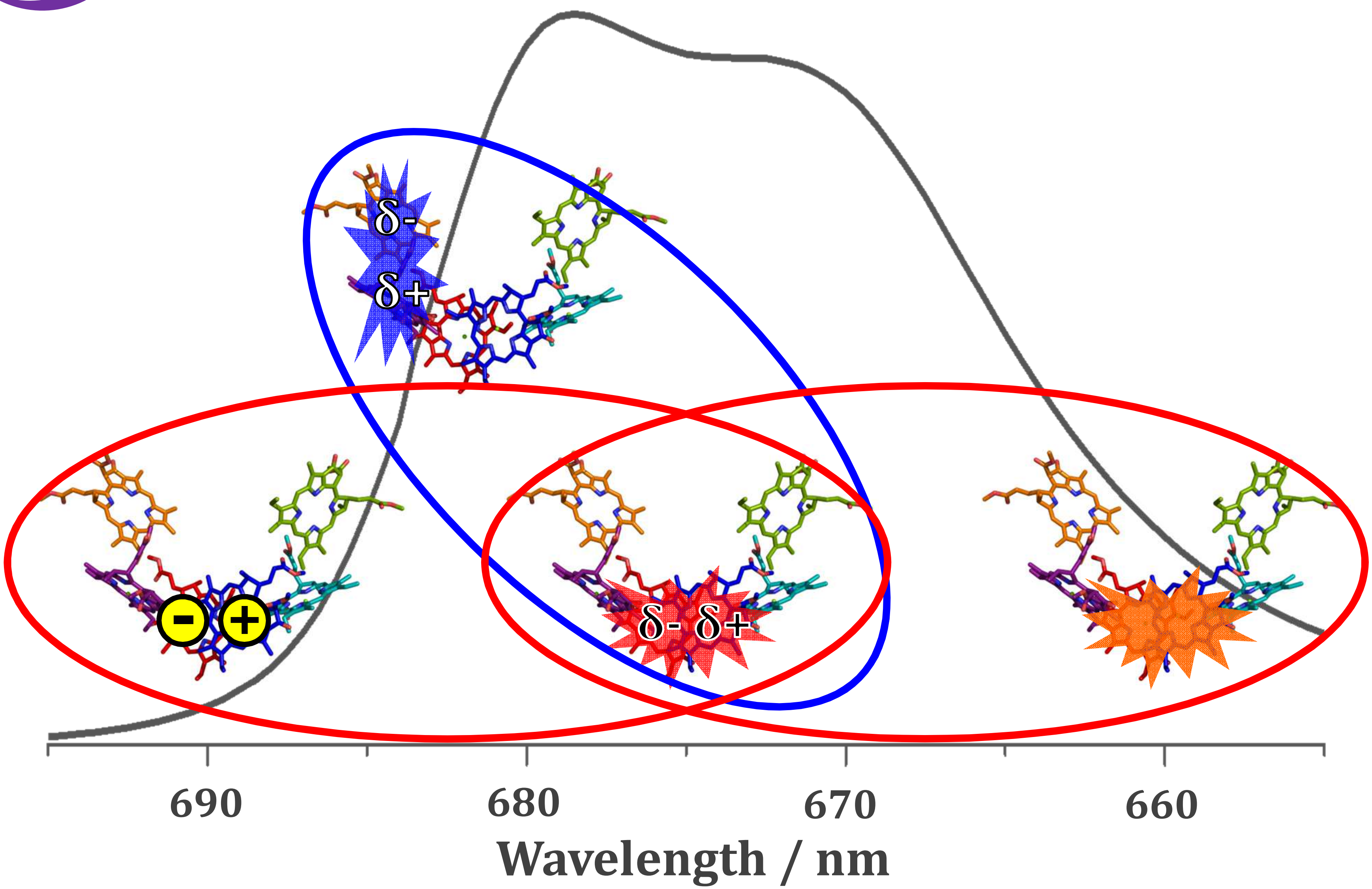
3rd Two Different (multiple) Charge Separation Pathways



P_{D1} path ***Chl_{D1} path***

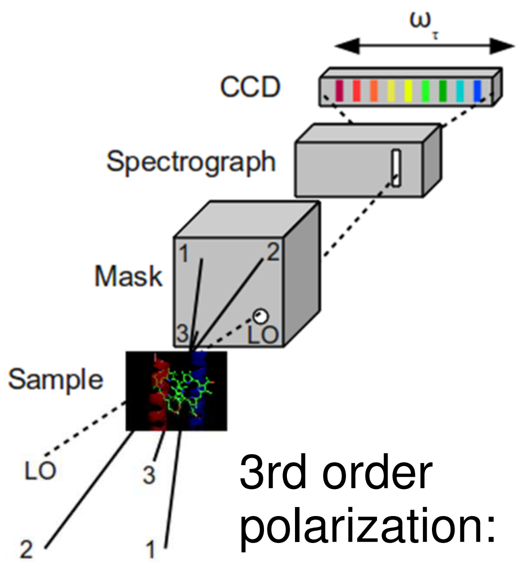
Romero et al, *Biochemistry*, **2010**
Novoderezhkin, Romero et al, *ChemPhysChem*, **2011**
Romero et al, *Biophysical Journal*, **2012**

4th Quantum Coherence



Romero et al, *Biophysical Journal*, **2012**

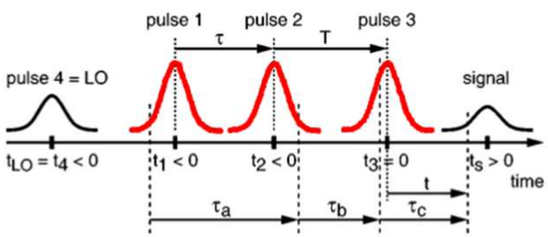
Two-Dimensional Electronic Spectroscopy

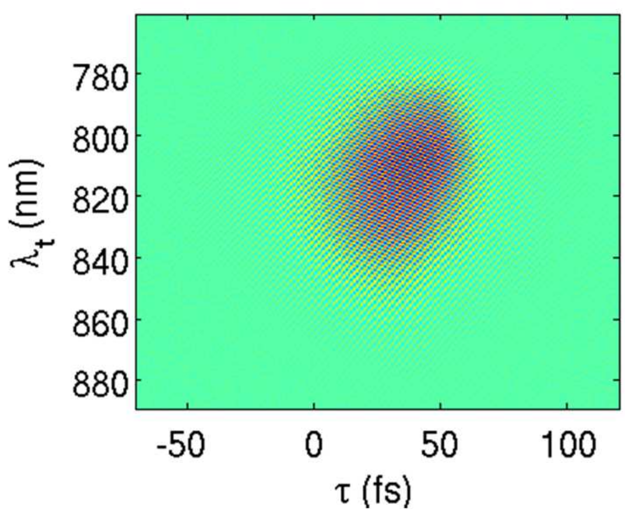


- 3 pulses (20 fs time duration)
- Non collinear geometry
- Phase matching: $k_s = -k_1 + k_2 + k_3$
- Heterodyne detection (amplitude + phase)
- Scan τ and T
- Sensitive to electronic and vibrational coherences

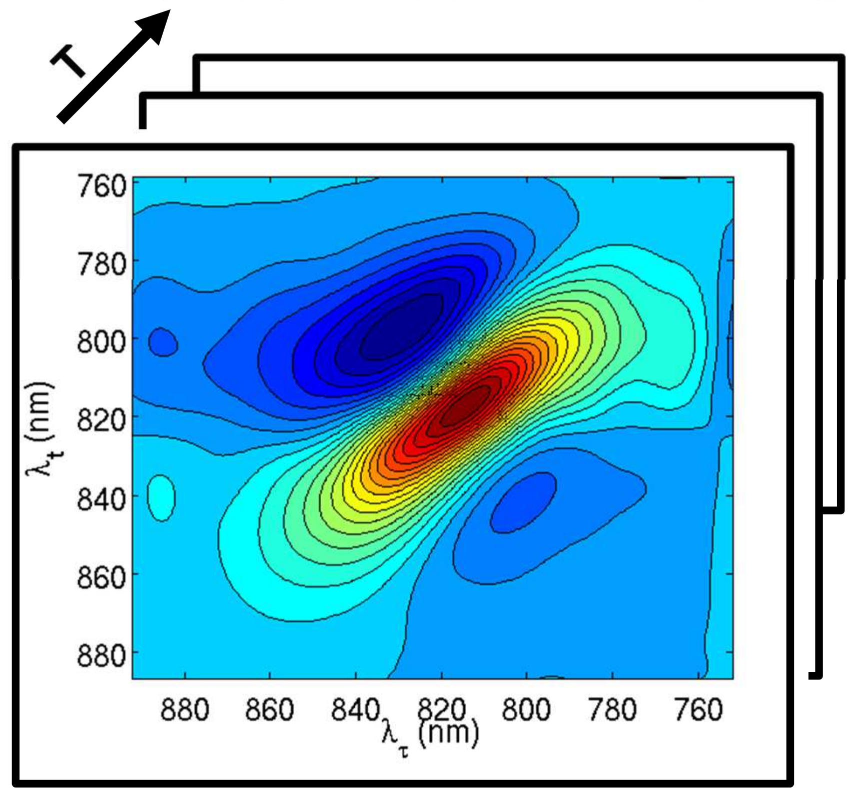
3rd order polarization:

$$P^{(3)}(t) = \left(-\frac{i}{\hbar}\right)^n \int_0^\infty dt_1 dt_2 dt_3 E(t-t_3)E(t-t_3-t_2)E(t-t_3-t_2-t_1)S^3(t_3, t_2, t_1)]$$

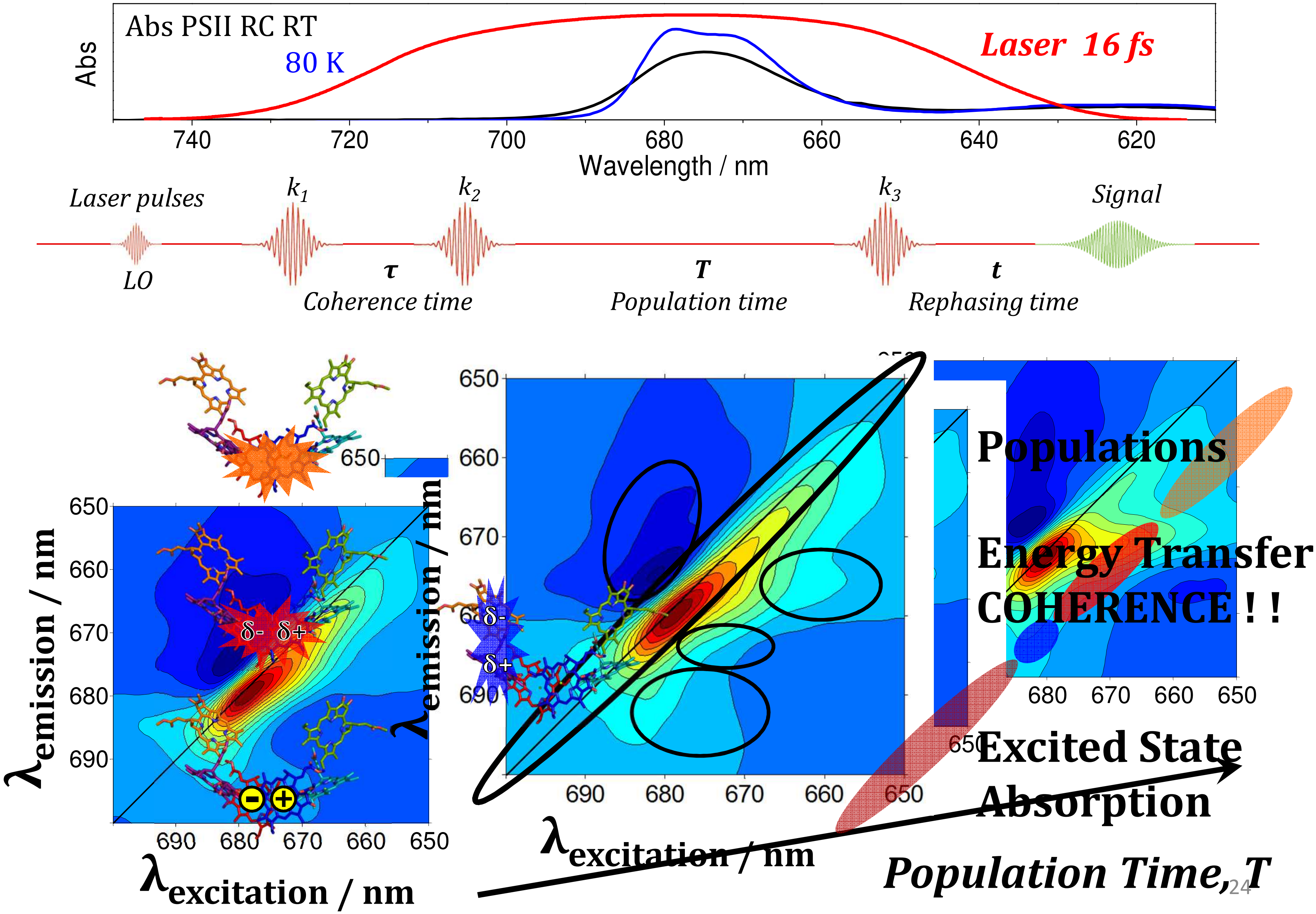




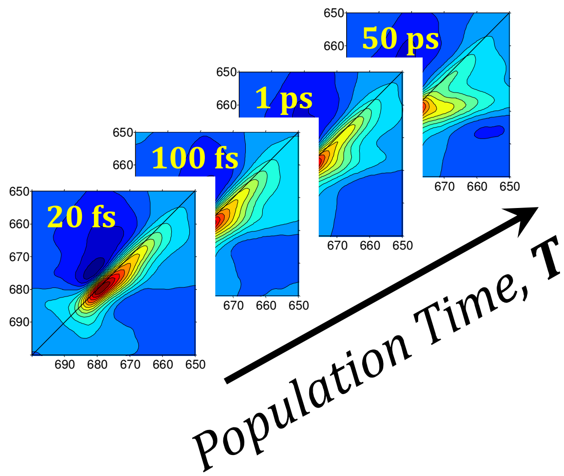
FT along τ

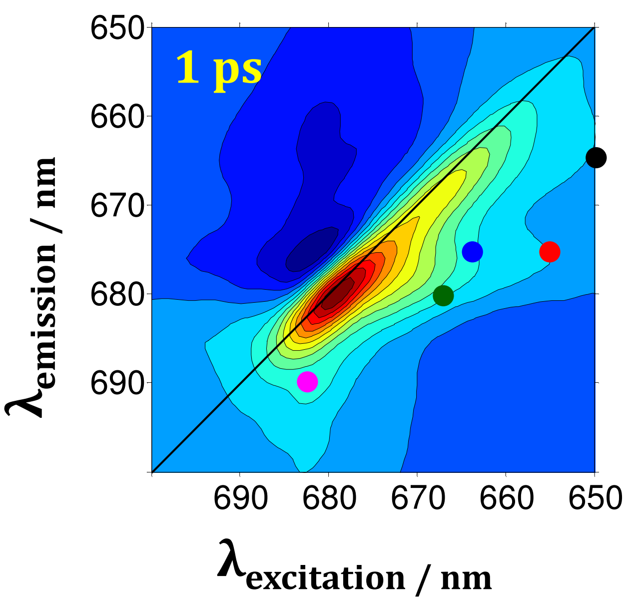


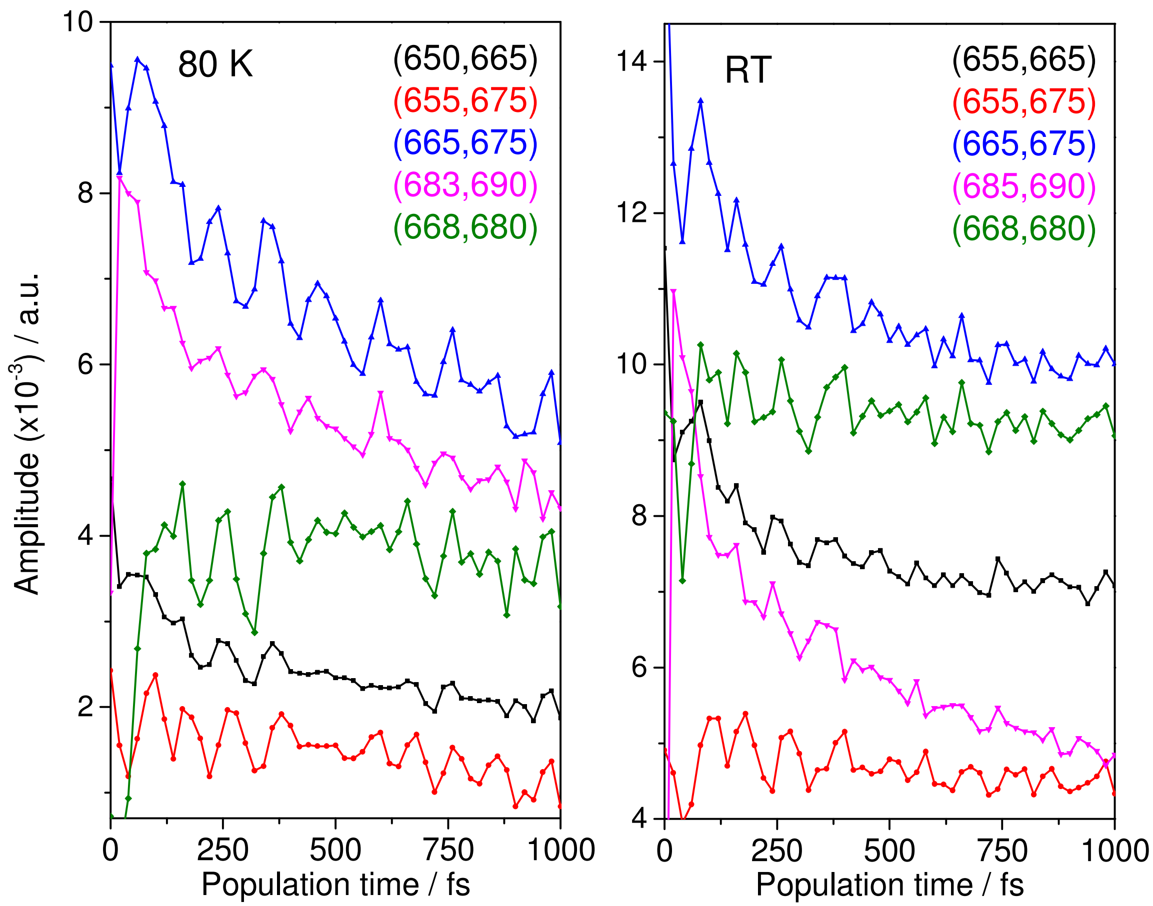
Two-Dimensional Electronic Spectroscopy



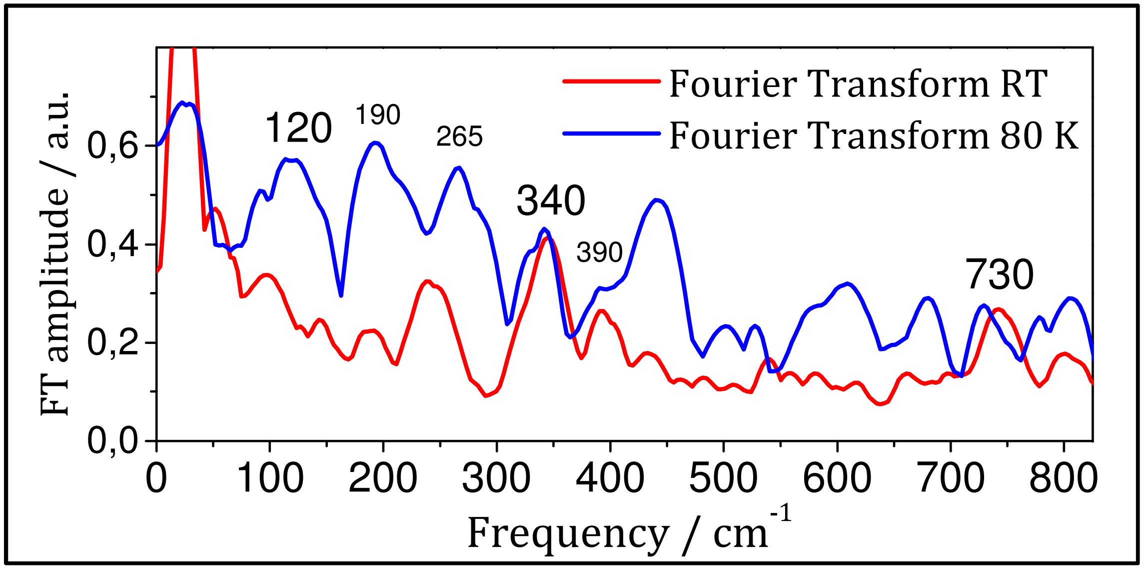
Quantum beats





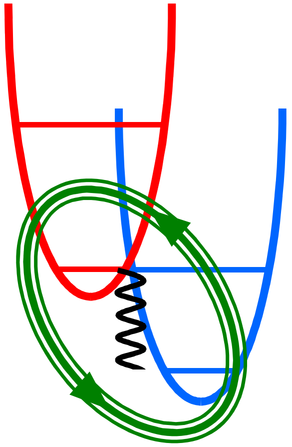


Fast Fourier Transform: 2D Frequencies



Chl *a* intramolecular vibrations

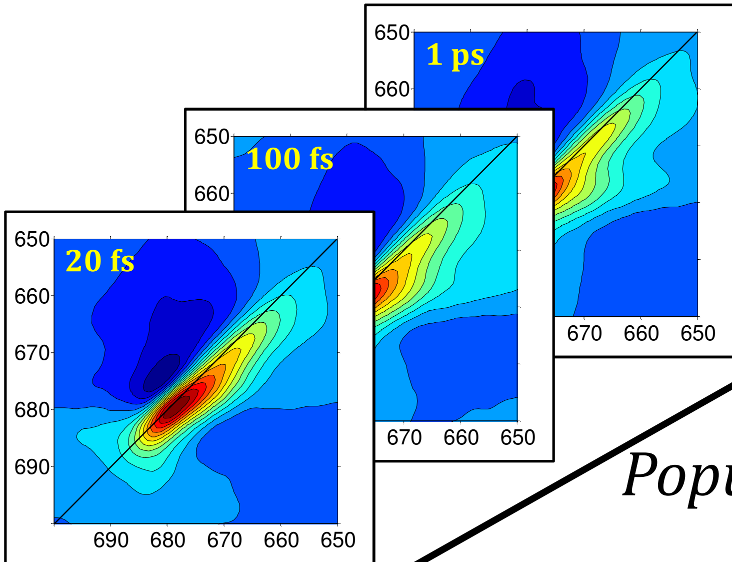
Optimal range
to match energy differences
between electronic states



Vibration-Assisted Electronic Coherence

Vibronic Coherence

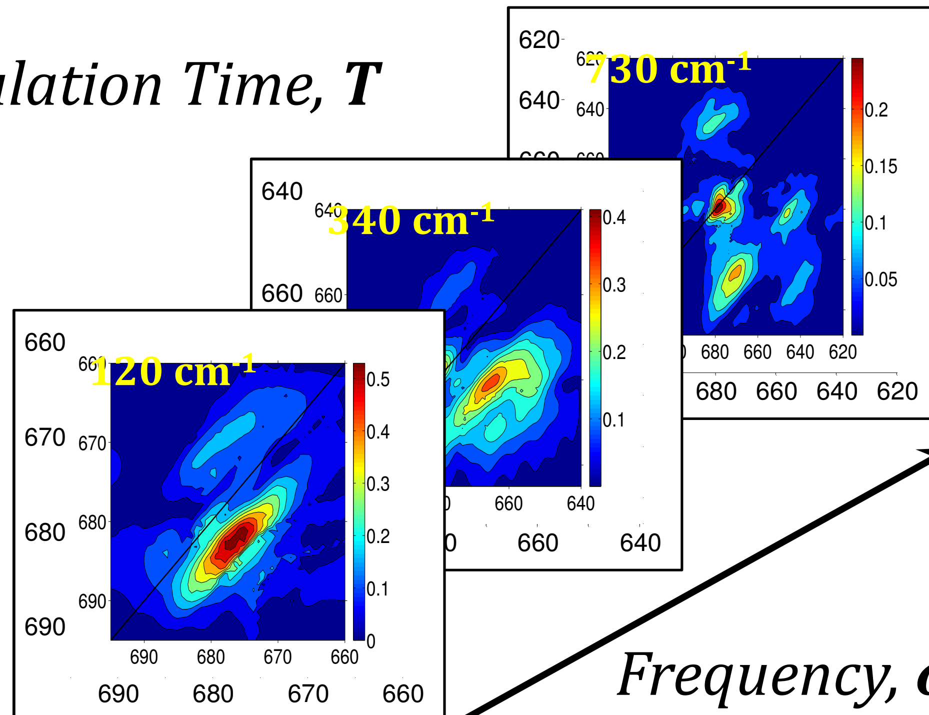
Fourier Transform: from Population Time to Frequency



*Population Time, **T***

2D spectra
All absorbing and emitting states

2D frequency maps
Only the states oscillating at certain frequency

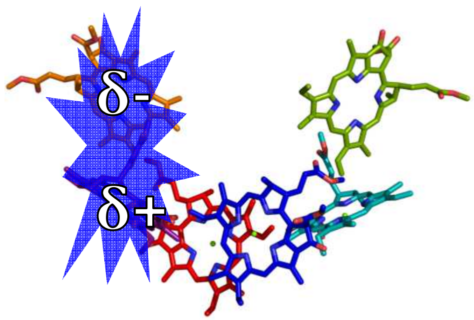


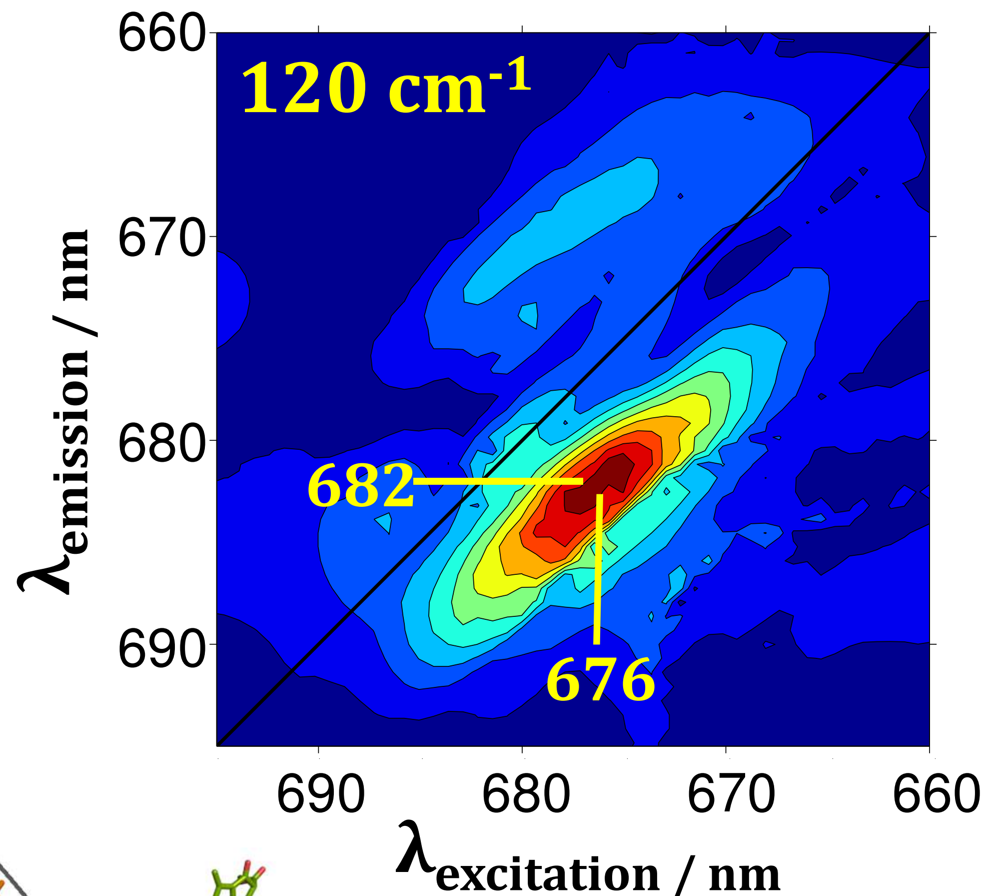
Frequency, $\boldsymbol{\omega_T}$

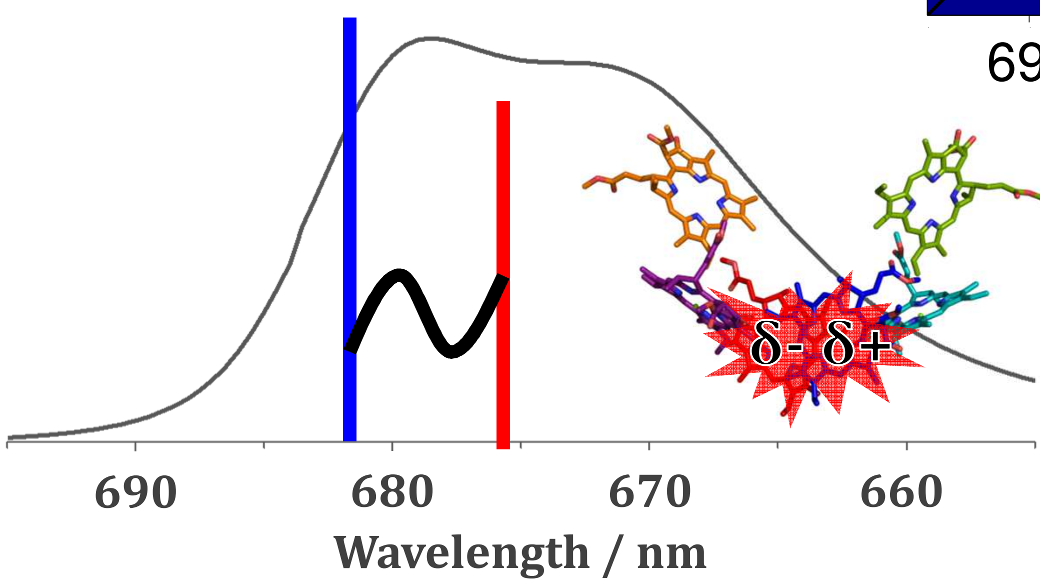
Fourier Transform

120 cm^{-1}

Sampling Energy Landscape



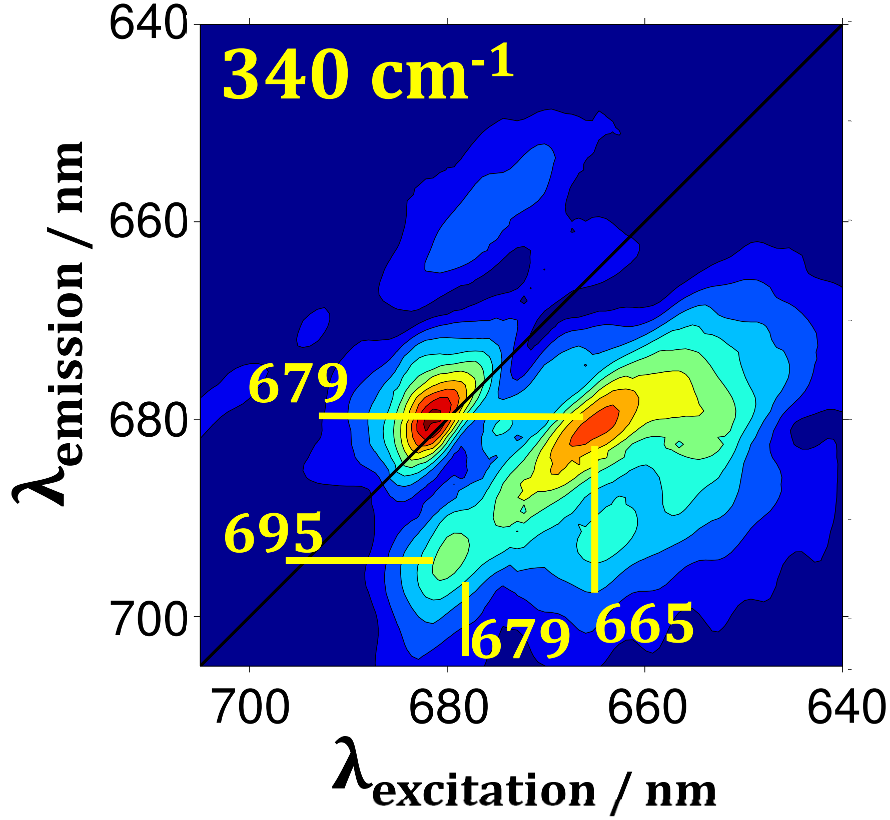




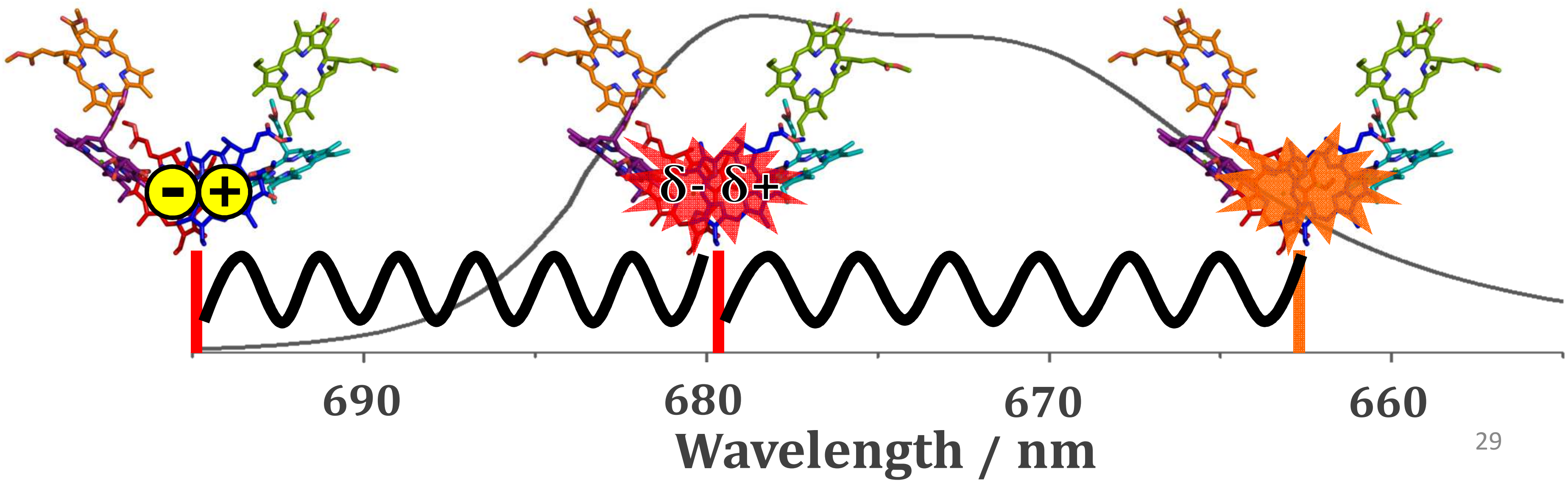
Romero et al,
Nature Physics, **2014**

340 cm⁻¹

Coherent electron transfer



Romero et al, *Nature Physics*, **2014**

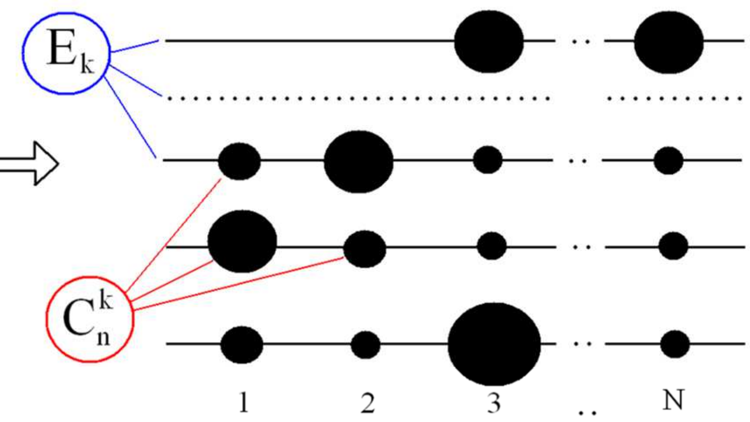


What is the Role of Quantum Coherence?

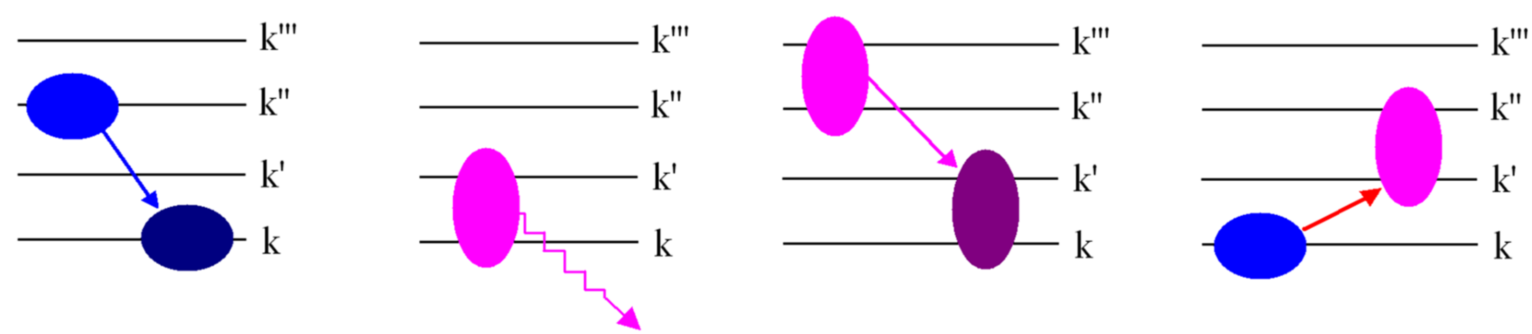
Disordered Exciton Redfield Model

1. Diagonalization of Hamiltonian —> exciton representation

$$\begin{vmatrix} E_1 & M_{12} & M_{13} \cdots\cdots & M_{1N} \\ M_{21} & E_2 & M_{23} \cdots\cdots & M_{2N} \\ \cdots & \cdots & \cdots & \cdots \\ M_{N1} & M_{N2} & \cdots\cdots & E_N \end{vmatrix} \Rightarrow$$



2. Density matrix equation



$\dot{p}_{kk} = R_{kkk''k''}\, p_{k''k''}$

population transfer

$\dot{p}_{kk'} = R_{kk'kk'}\, p_{kk'}$

decay of coherence

$\dot{p}_{kk'} = R_{kk'k''k'''}\, p_{k''k'''}$

coherence transfer

$\dot{p}_{k'k''} = R_{k'k''kk}\, p_{kk}$

population to coherence transfer

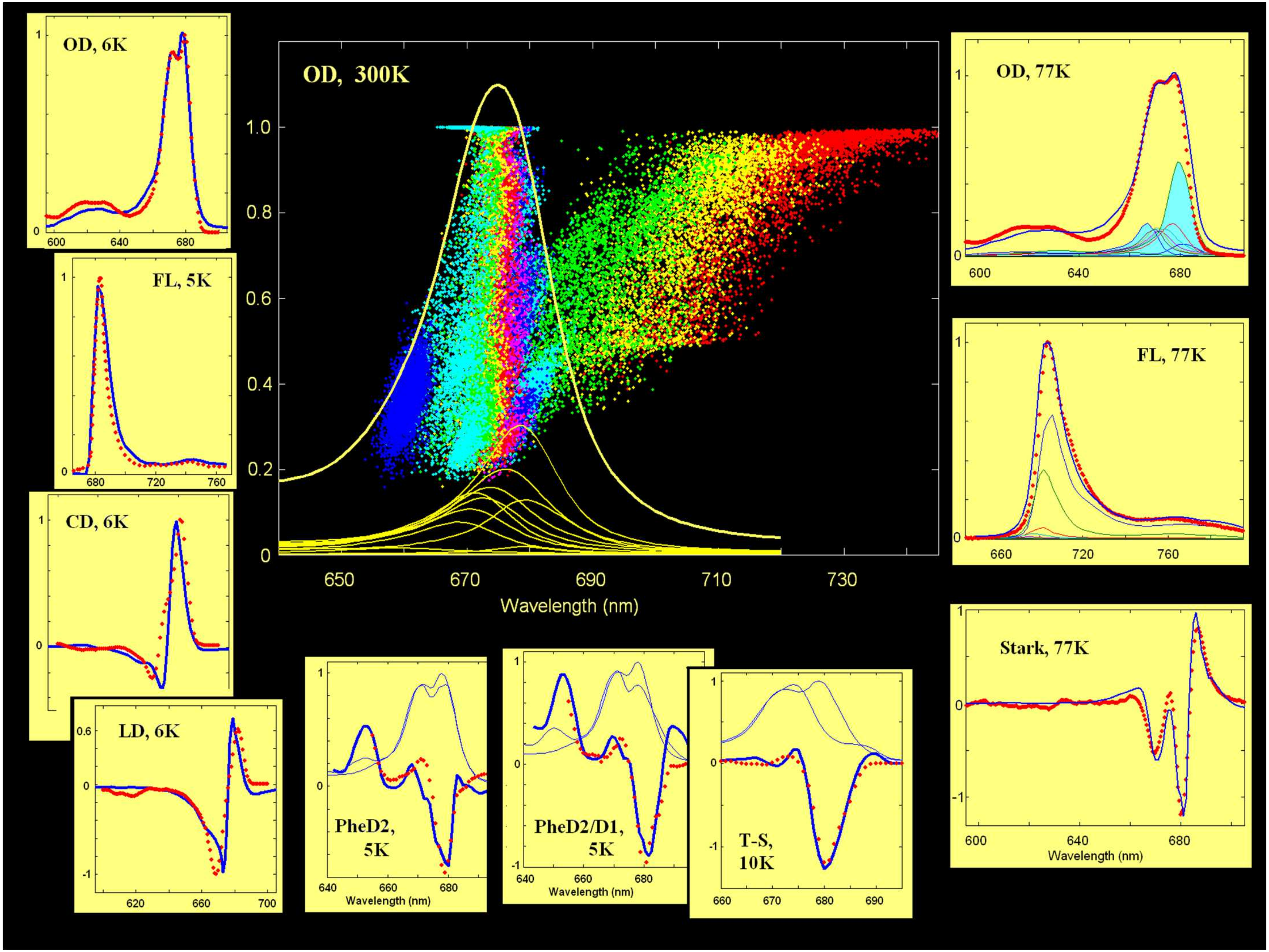
3. Redfield relaxation tensor

$$R_{kkk''k''} = \sum_n (C_n^k C_n^{k''})^2 J(\omega_{kk''})$$

population transfer

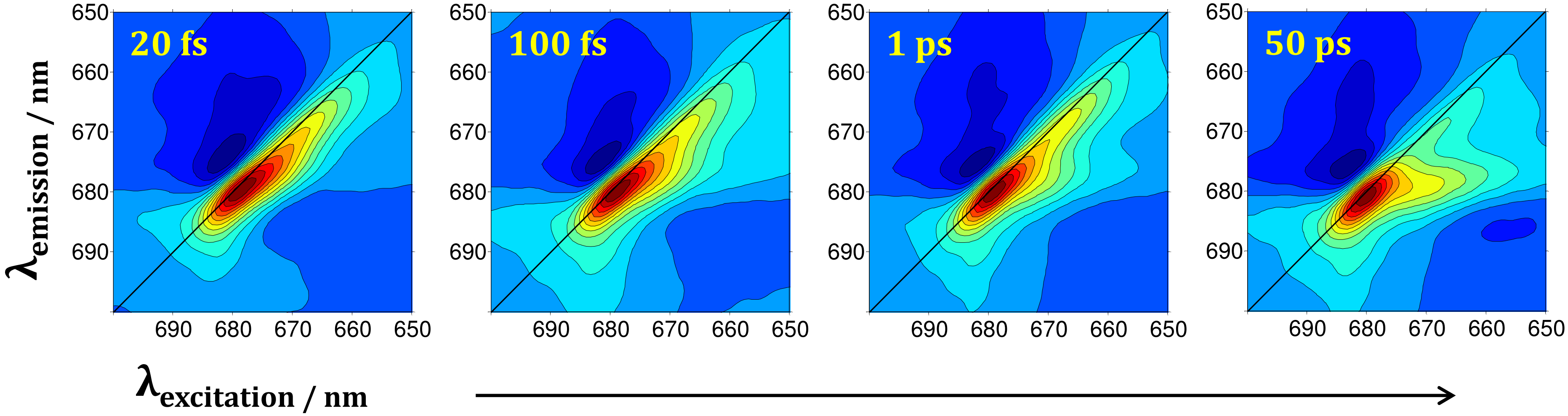
exciton wavefunctions overlap

exciton-phonon spectral density

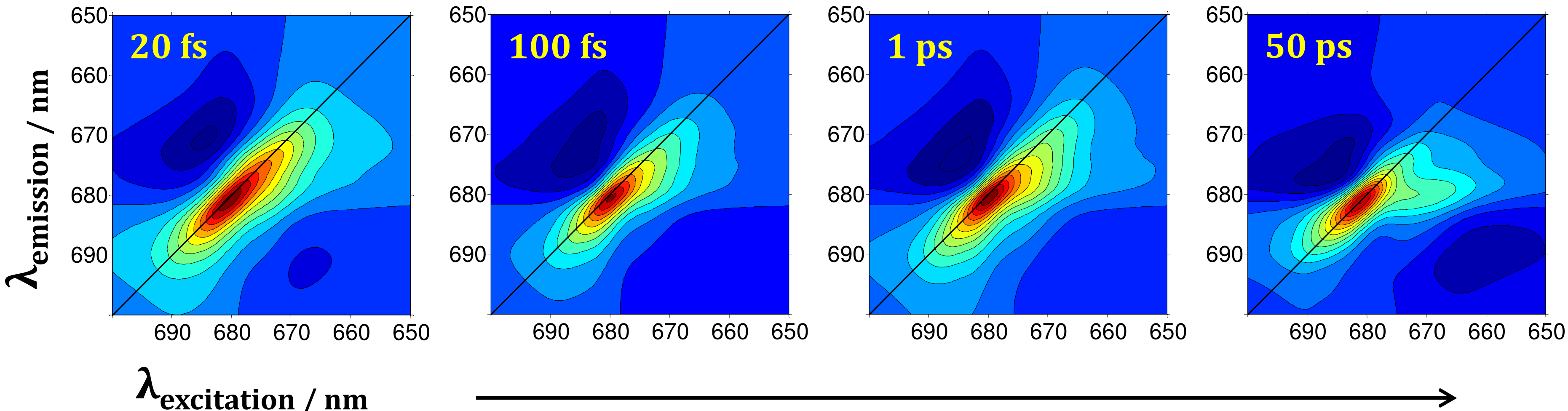

OD, 300K
Wavelength (nm)
OD, 6K
FL, 5K
CD, 6K
LD, 6K
PheD2,
5K
PheD2/D1,
5K
T-S,
10K
OD, 77K
FL, 77K
Stark, 77K

Disordered exciton - Charge-Transfer Redfield Model

Experimental



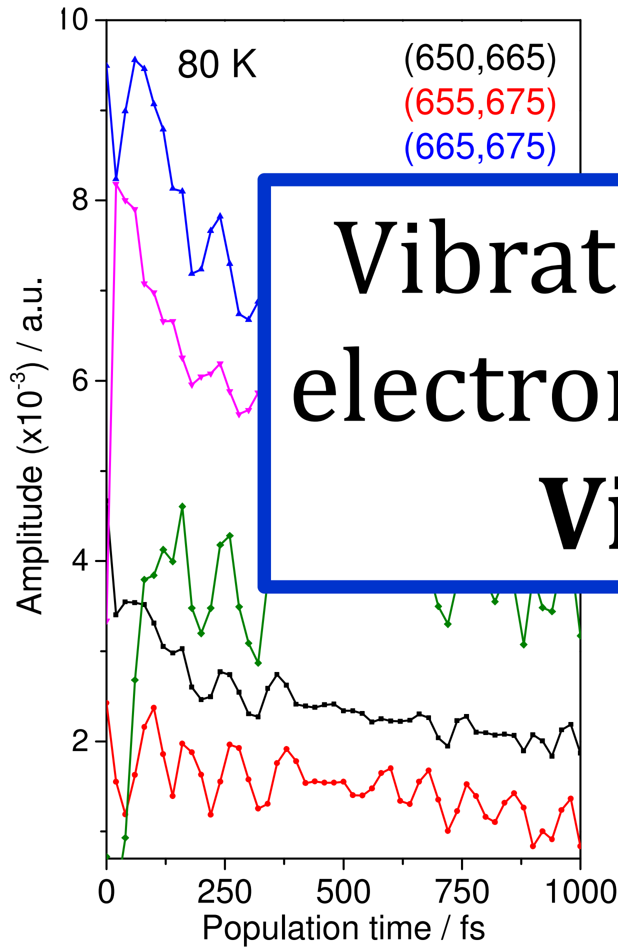
Calculated



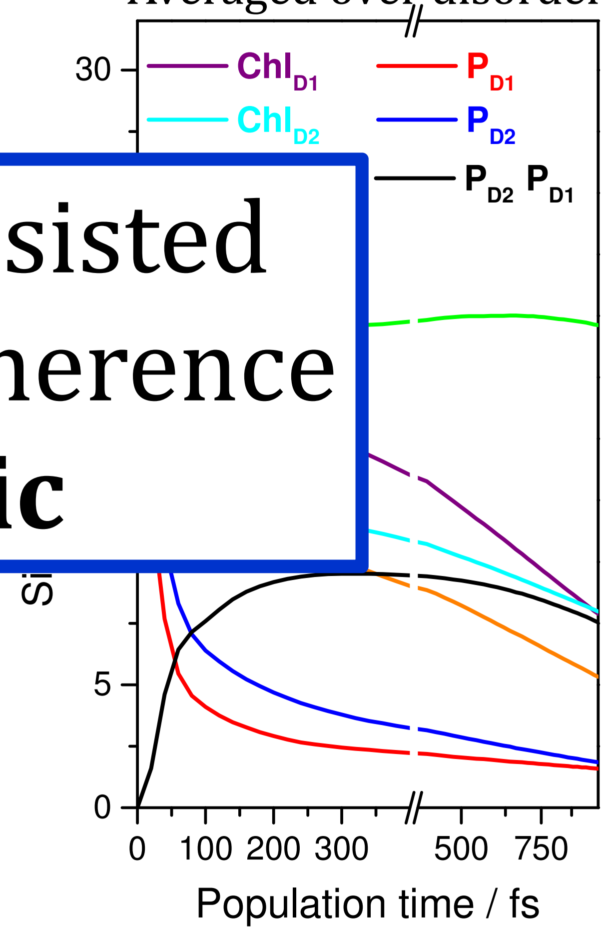
Quantum Beats

Experiment *vs.* *Model*

Beats up to 1 ps ***Beats up to 400 fs***



Averaged over disorder



Vibration-assisted electronic coherence

Vibronic

5th

Good Vibrations

Vibration-Assisted Electronic Coherence

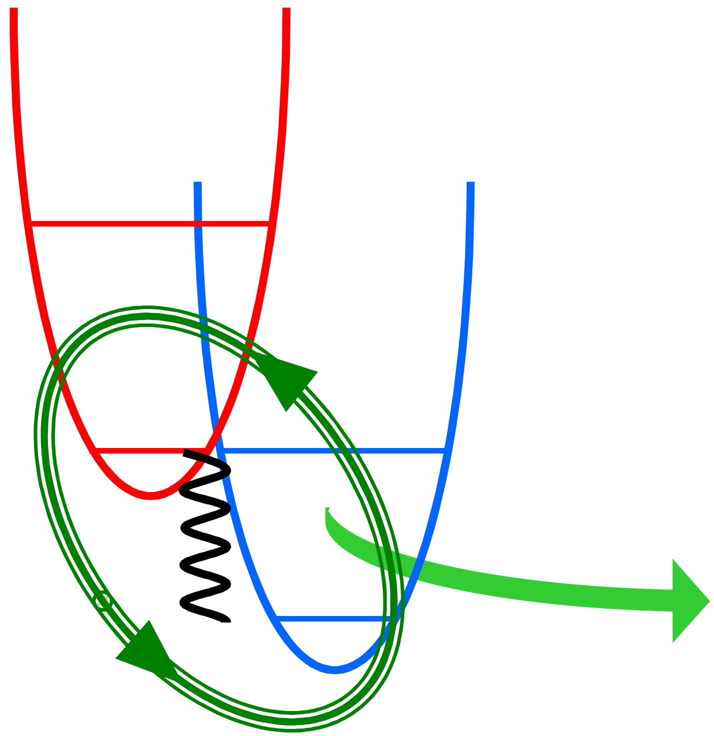
Vibronic Coherence

key parameters
leading to coherence

Electronic Energy Levels

Vibrational Modes

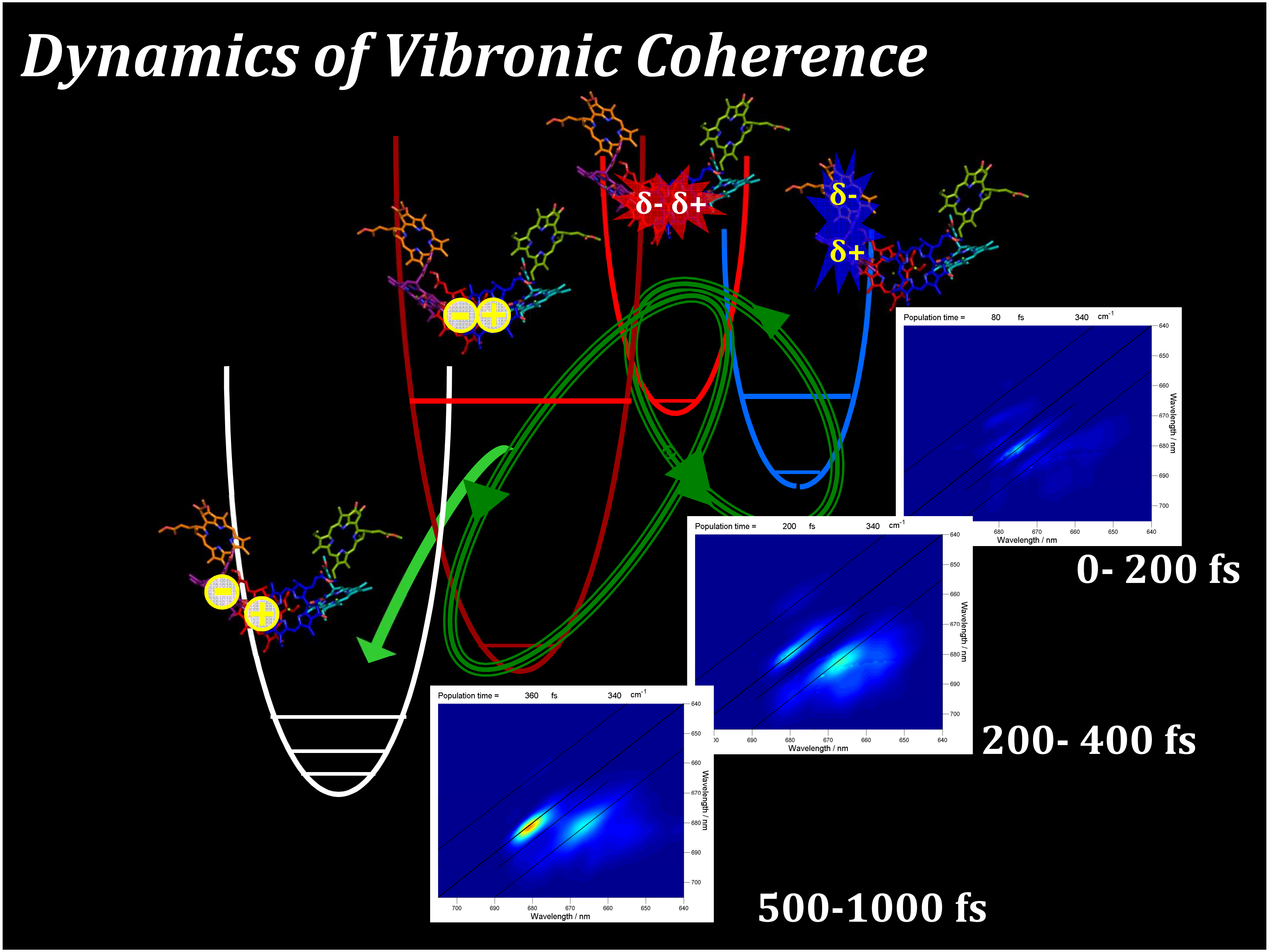
Resonance !!!!



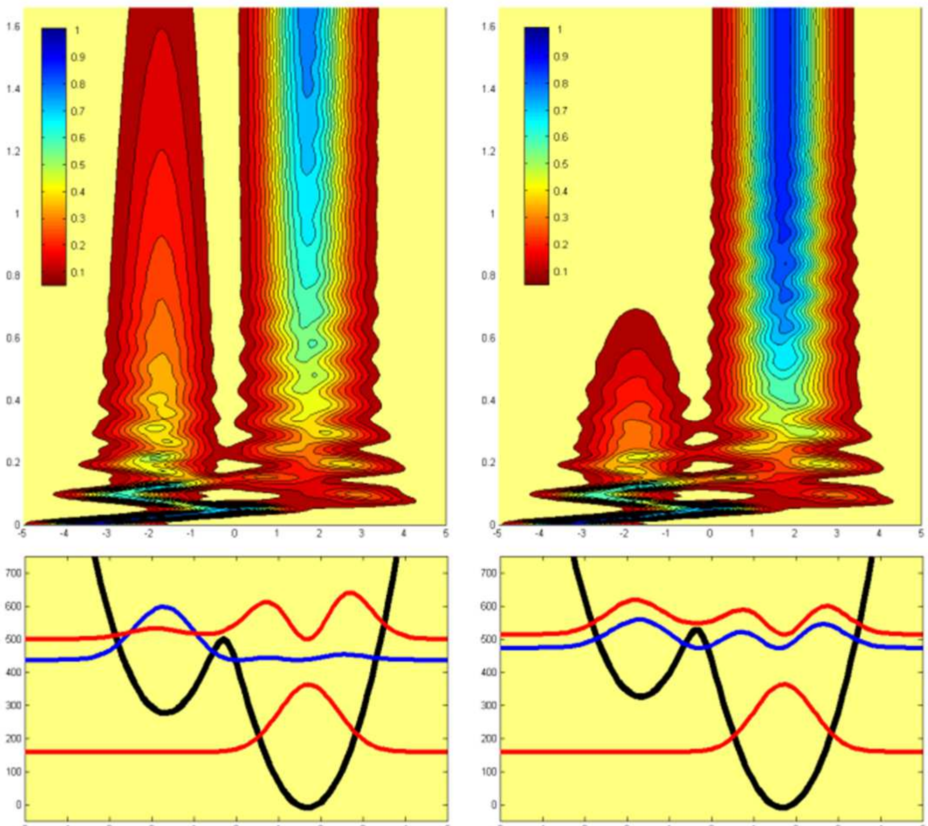
Advantages
Speed
Directionality

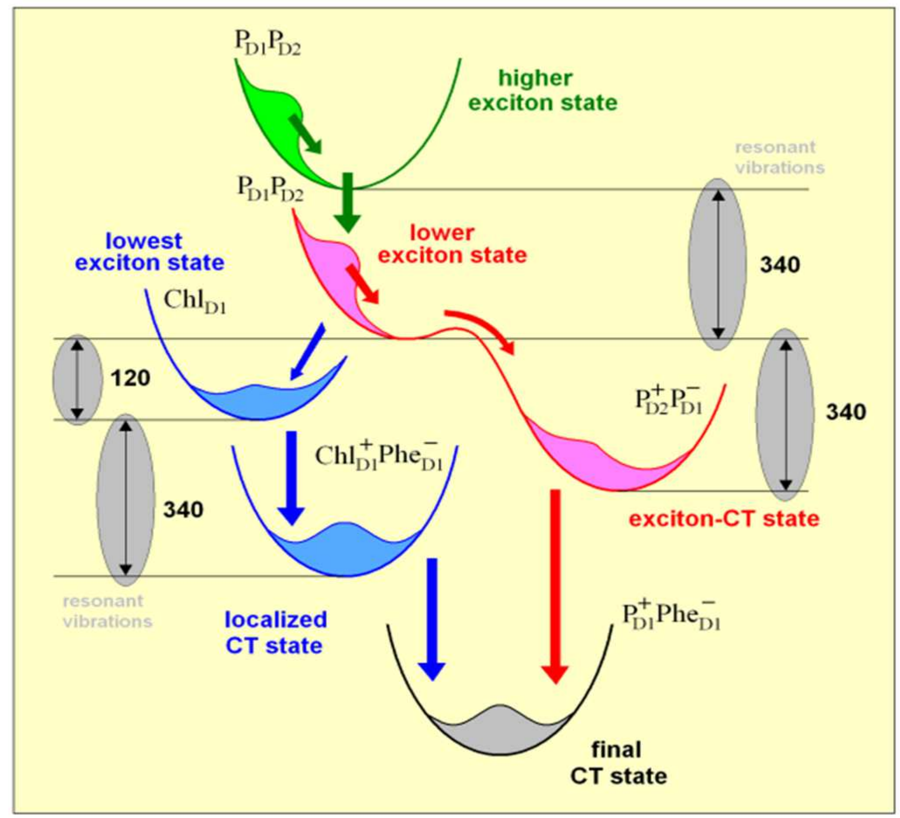
Efficiency

coupling to Phonon bath


Dynamics of Vibronic Coherence
δ- δ+
δ-
δ+
Population time = 80 fs 340 cm-1
Wavelength / nm
0- 200 fs
Population time = 200 fs 340 cm-1
Wavelength / nm
200- 400 fs
Population time = 360 fs 340 cm-1
Wavelength / nm
500-1000 fs

How resonant vibrations promote efficient charge separation



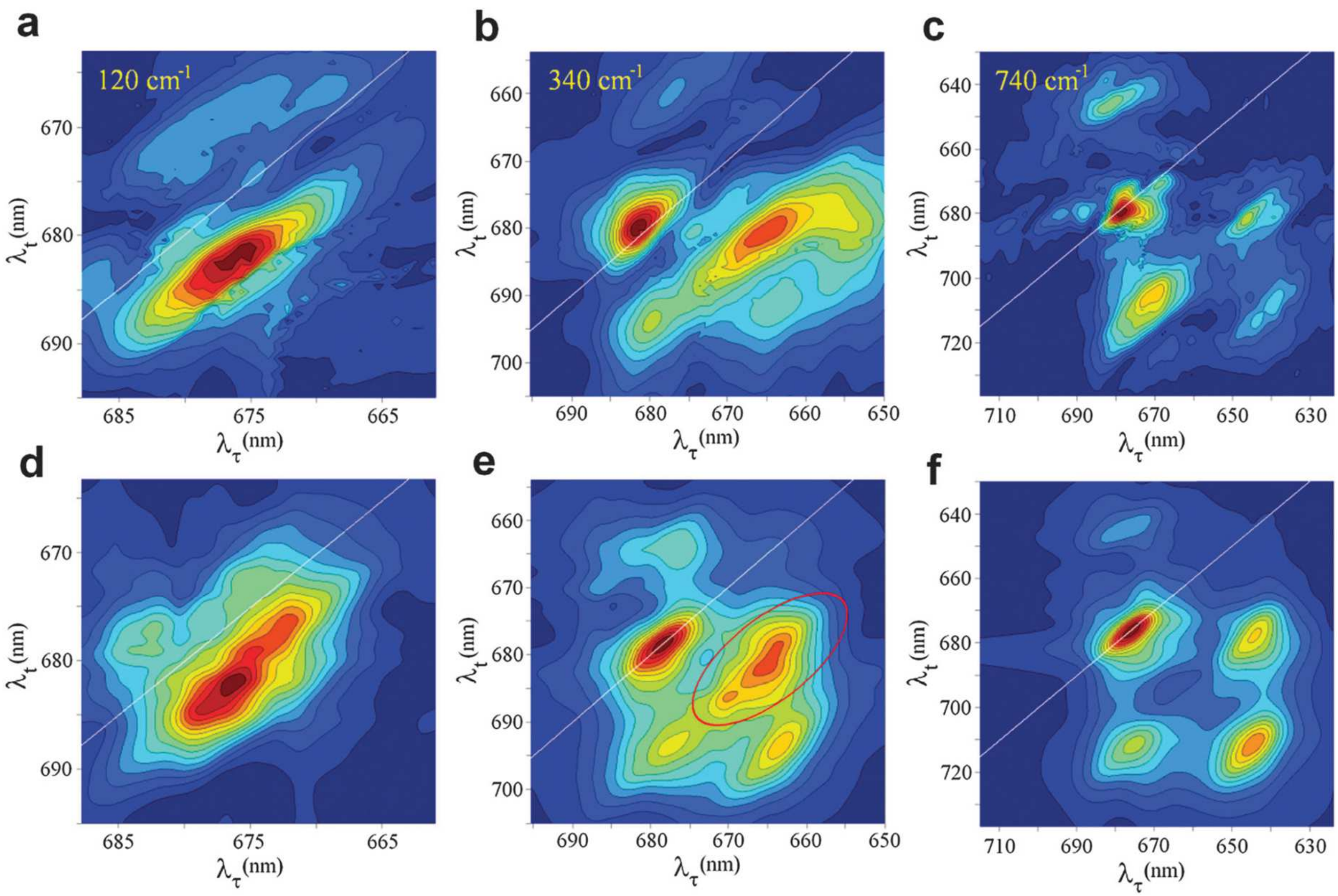


PCCP

Cite this: DOI: 10.1039/c5cp00582e

How exciton-vibrational coherences control charge separation in the photosystem II reaction center†

Vladimir I. Novoderezhkin,*[a] Elisabet Romero[b] and Rienk van Grondelle[b]



6th

Light Harvesting:

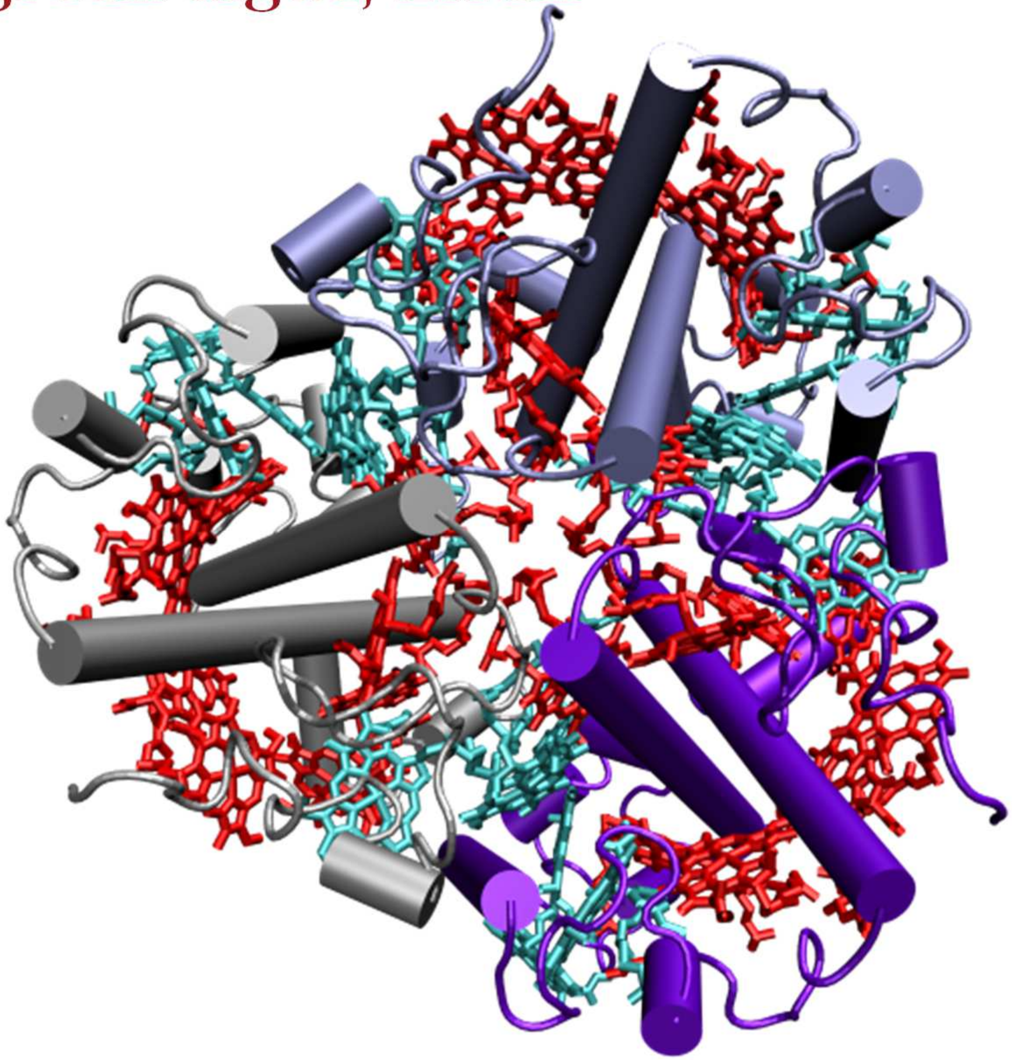
Excitons and Dark States

And

Photoprotection

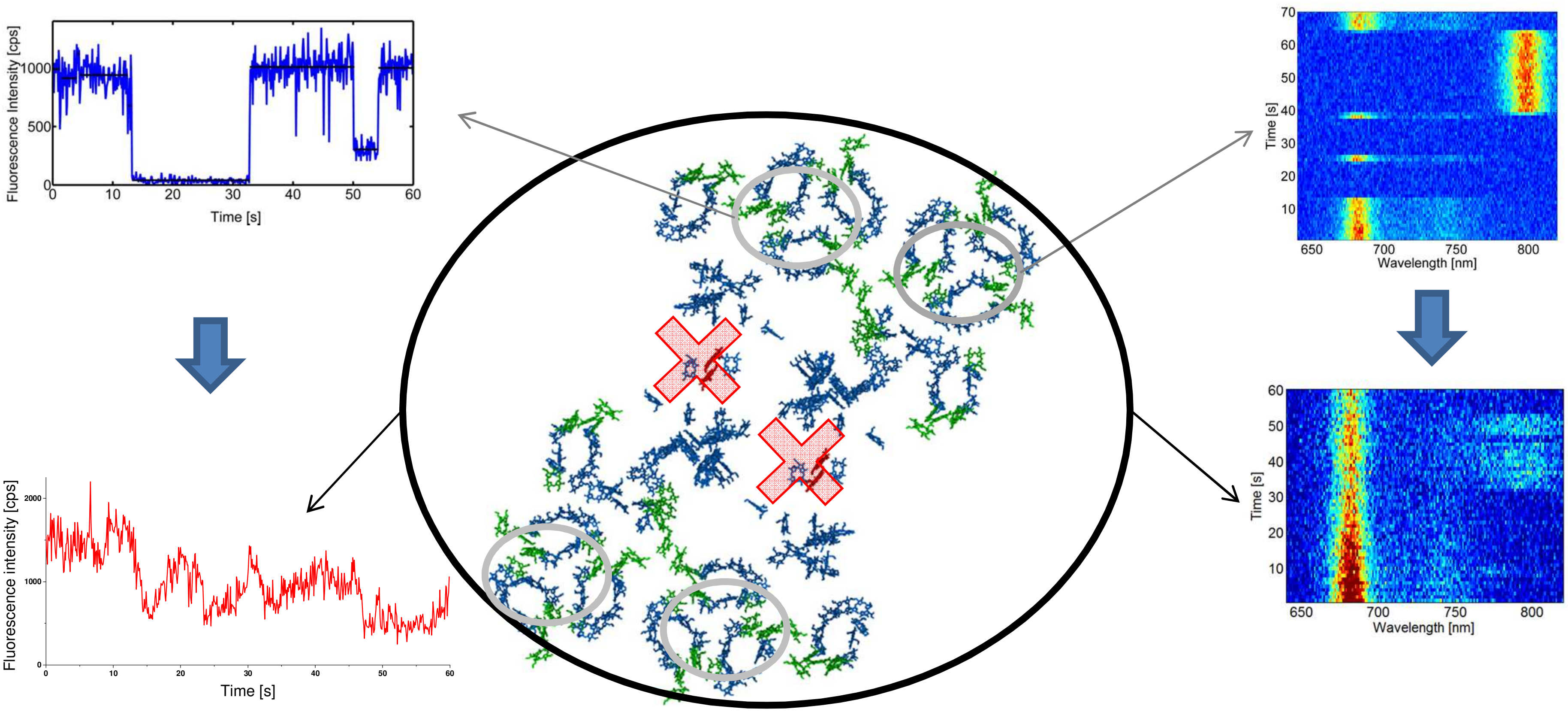
chromophores at 0.5 M

in the major light-harvesting complex of higher plants & green algae, LHCII

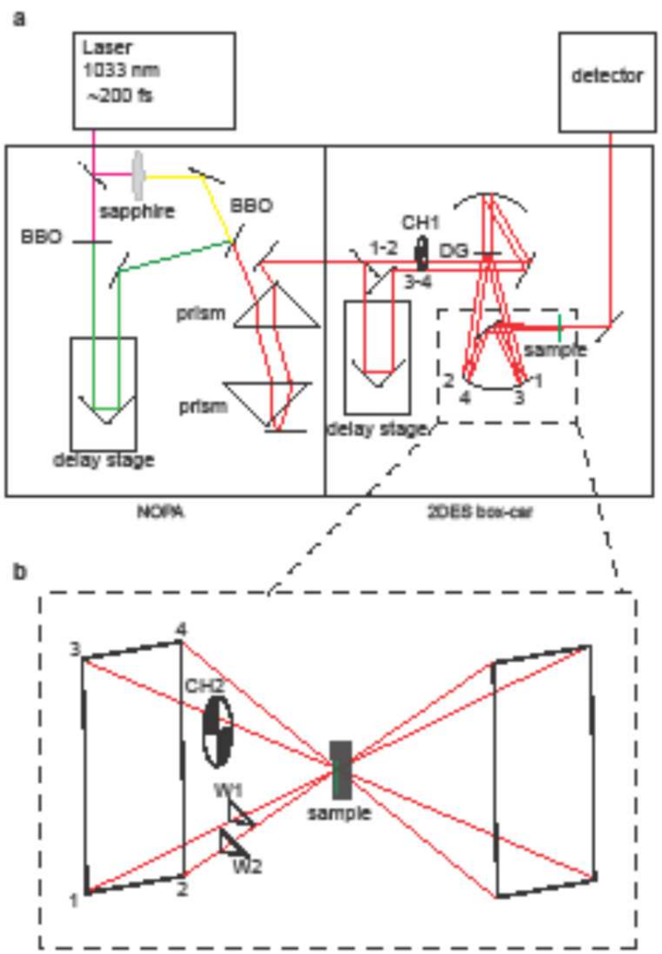


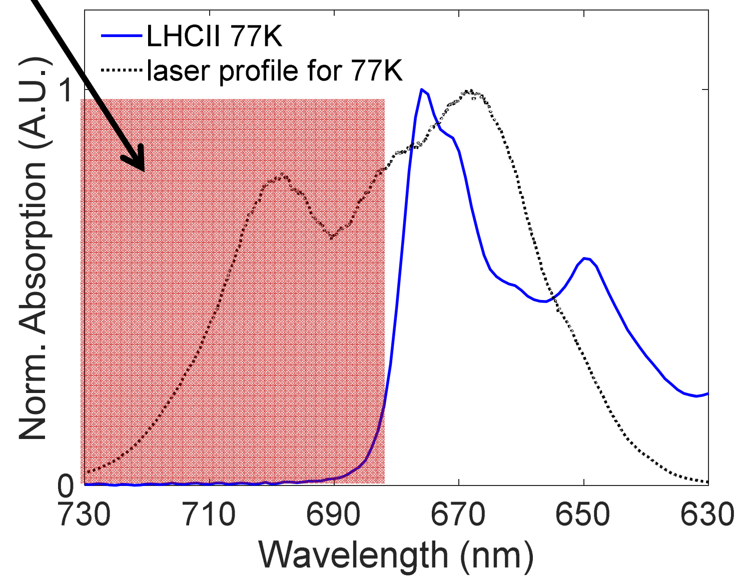
- no concentration quenching

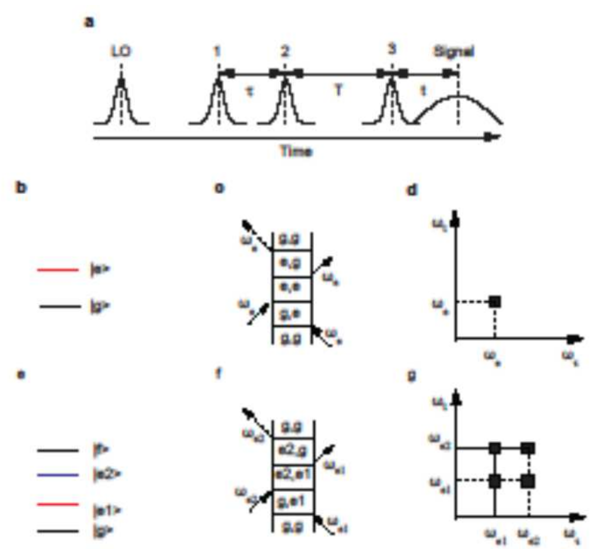
Blinking, quenching, trapping, S-T annihilation in PS2 supercomplexes



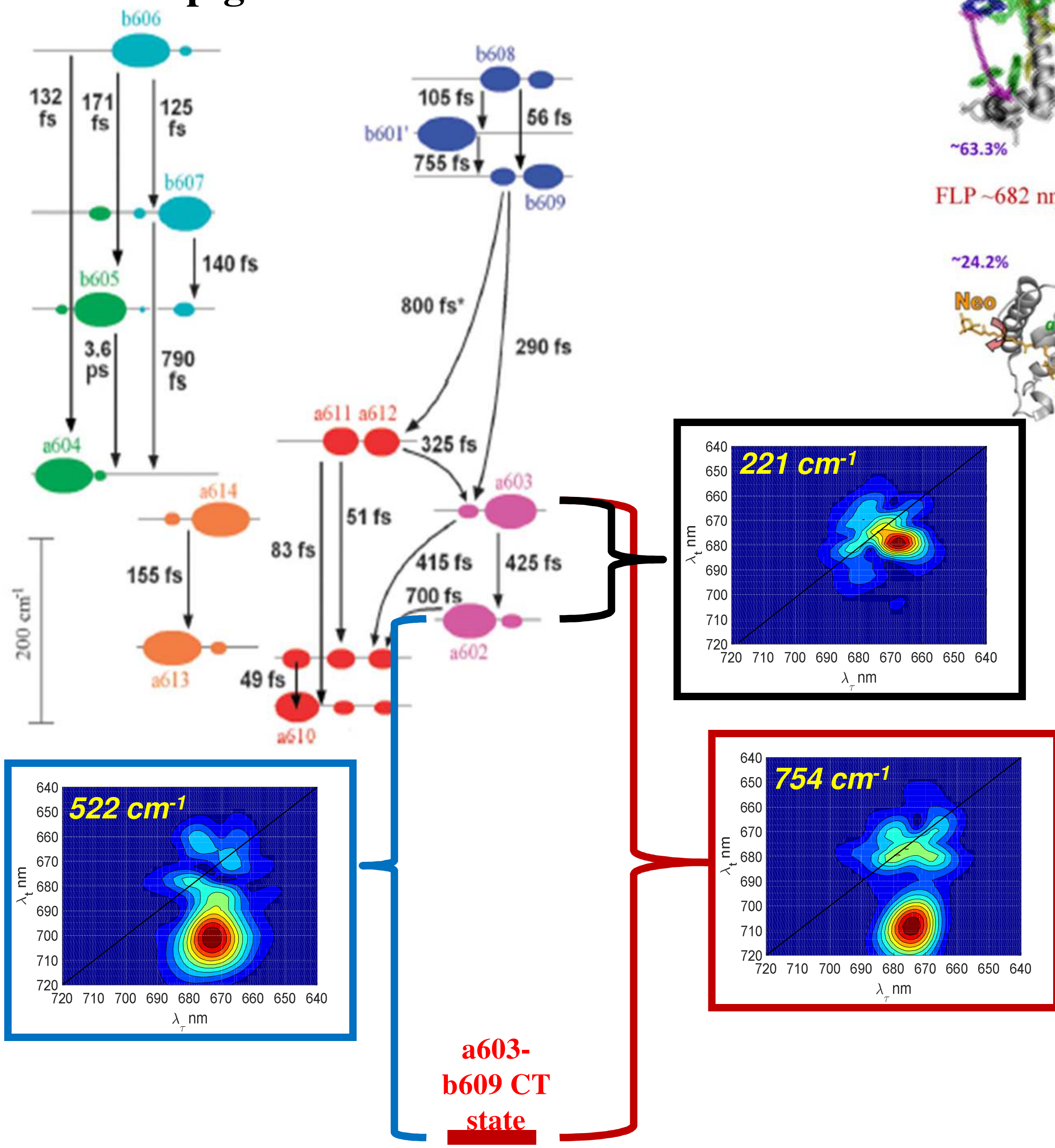
Laser aligned to probe low energy states on the red side of the Q_y.

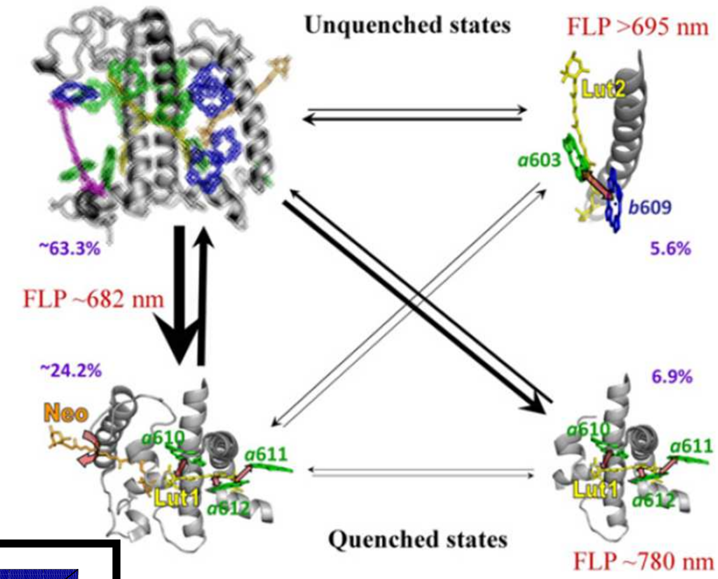






Excitonic manifold of Chl *a* and *b* pigments in LHCII

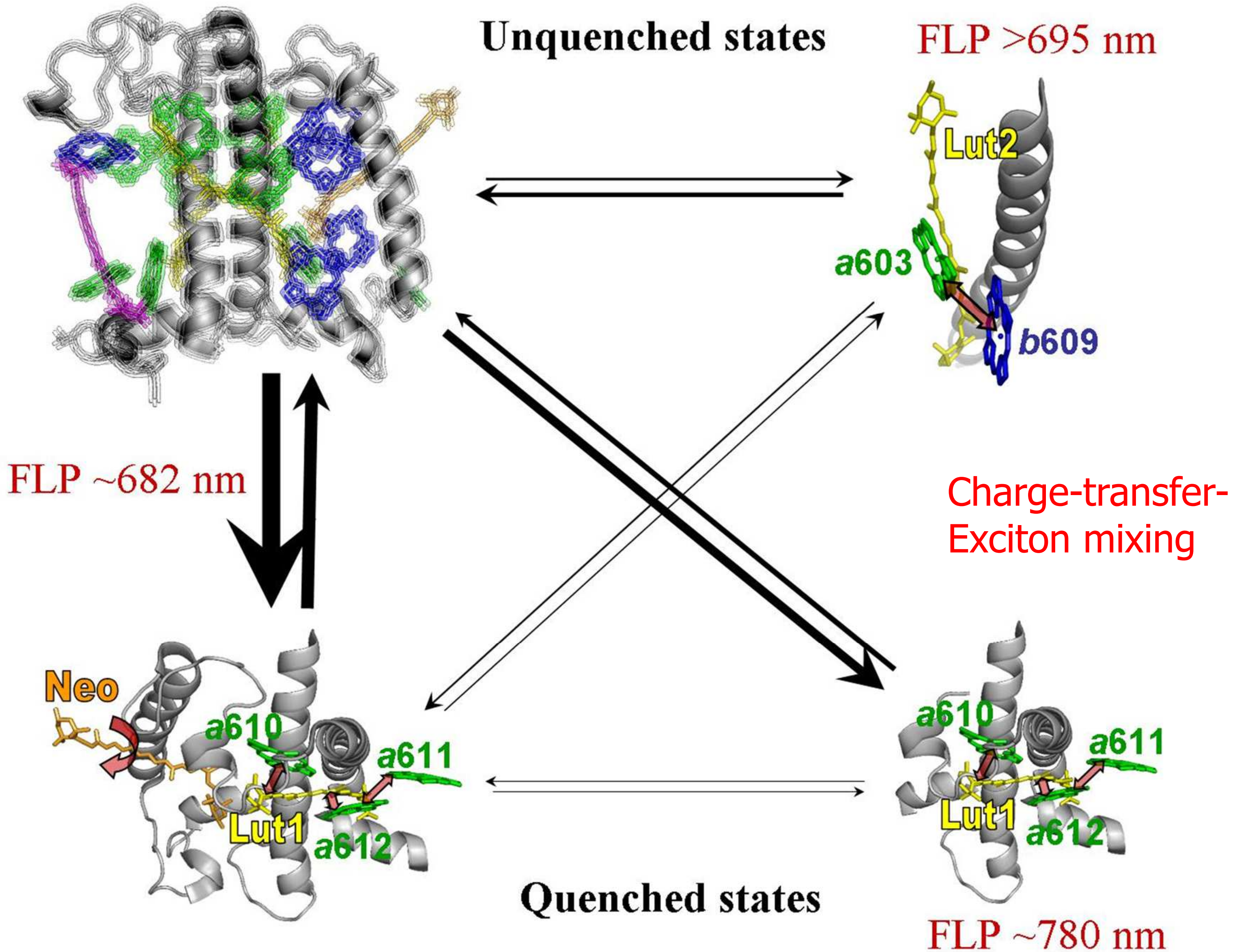




Dynamic coherence between *a*603-*b*609 CT state and *a*602-*a*603 dimer

Novoderezhkin, V., Marin, A. & van Grondelle, R. *Phys. Chem. Chem. Phys.* **13,** 17093–17103 (2011).
Kruger, T. P. J. *et al. Biophys. J.* **102,** 2669–2676 (2012).

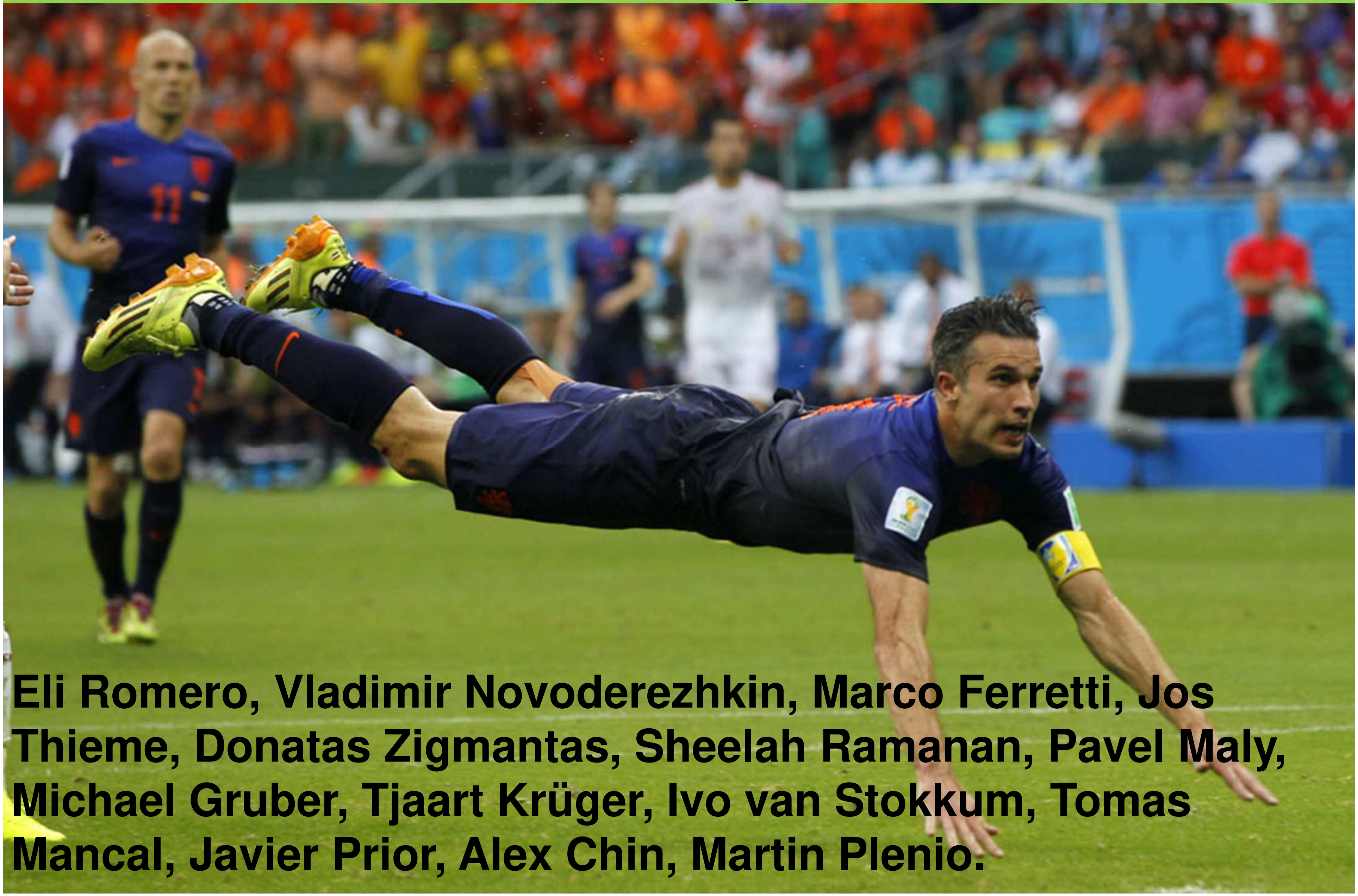
Environmentally controlled disorder



Krüger *et al. Biophys J* 102:2669 (2012)


Quantum Design of a Light Trap
1. Excitons (mobile, delocalized)
2. Charge Transfer (mixed with excitons)
3. Multiple Pathways
4. Coherence and Speed
5. Good Vibrations
6. Dark States
7. Control
SMART
PROTEIN

Acknowledgements



Eli Romero, Vladimir Novoderezhkin, Marco Ferretti, Jos Thieme, Donatas Zigmantas, Sheelah Ramanan, Pavel Maly, Michael Gruber, Tjaart Krüger, Ivo van Stokkum, Tomas Mancal, Javier Prior, Alex Chin, Martin Plenio.