Energy Transfer Pathways in PSI-LHCI probed by Two-Dimensional Electronic Spectroscopy

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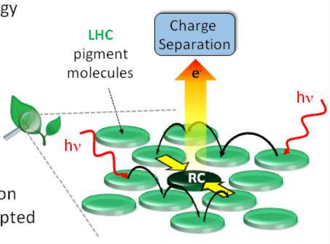
Introduction

Photosynthesis converts solar energy into chemical energy in a very efficient way thanks to Photosystems.

Photosystem:
Light Harvesting Complex (LHC) serves as antenna to absorb the solar energy and induce an energy transfer process towards the **Reaction Center** (RC) where the charge separation takes place.

This process happen at ultrafast time scale. For this reason **Two-Dimensional Electronic Spectroscopy** (2DES) is adopted to investigate the energy transfer pathways.

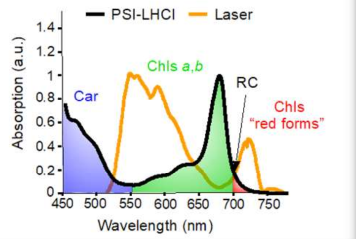


The Sample

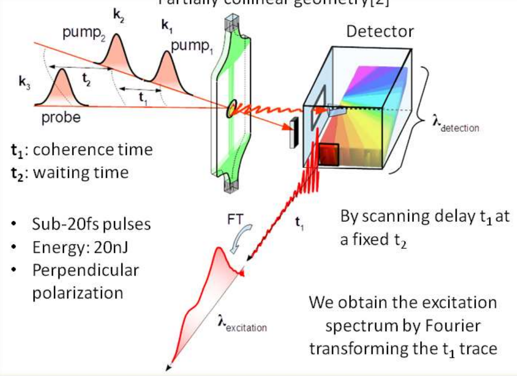
Photosystem I (PSI) has a very high quantum conversion efficiency (>95%). In land plants it is combined with the peripheral LHCI [1]

PSI-LHCI isolated from spinach and treated with $Fe(CN)_6$ to avoid the charge separation in RC.

Pigments: Carotenoids (Car), Chlorophylls (Chls) *a*,*b* and Chl «red forms» (absorption 710 -730 nm) at lower energy with respect the primary donor of RC (700 nm).



Experimental method: 2DES



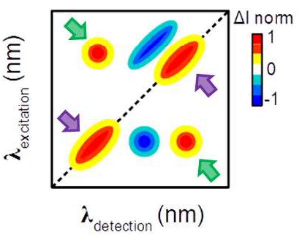
t_1: coherence time
t_2: waiting time

- Sub-20fs pulses
- Energy: 20nJ
- Perpendicular polarization

By scanning delay t_1 at a fixed t_2

We obtain the excitation spectrum by Fourier transforming the t_1 trace

2D absorption spectrum is obtained by collecting the excitation spectra per each detection wavelengths



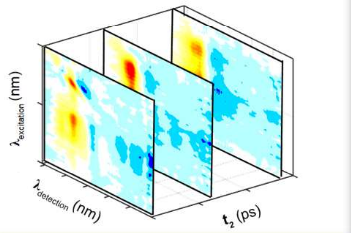
Diagonal peaks: reflect the linear absorption Properties (homogeneous and inhomogeneous broadening)

Cross peaks: Contain contributions from coupled system/Energy Transfer (EET) processes

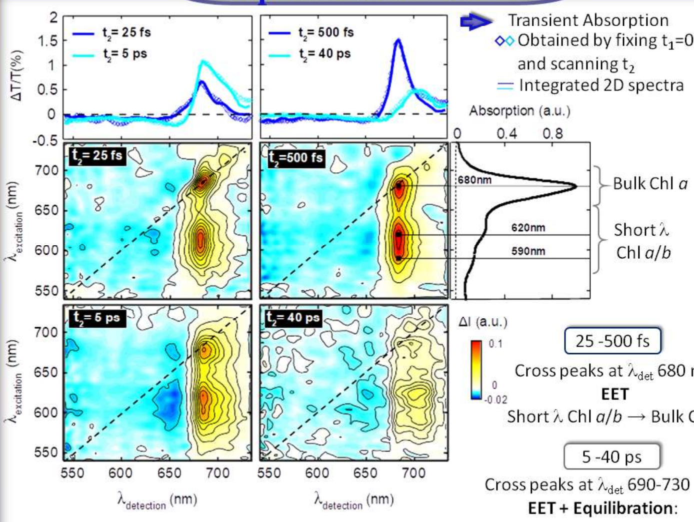
Negative peaks reflect the excited states absorption [3]

By scanning delay t_2 we obtain a collection of 2D spectra that show the temporal evolution of each excitation/detection point

$$S(\lambda_{exc}, t_2, \lambda_{det})$$



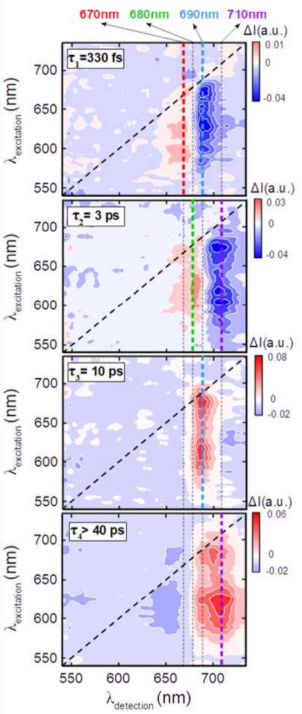
Experimental Results



25 -500 fs
Cross peaks at λ_{det} 680 nm
EET
Short λ Chl *a/b* → Bulk Chl *a*

5 -40 ps
Cross peaks at λ_{det} 690-730 nm
EET + Equilibration:
Bulk Chl *a* → Chls red forms

Data Analysis



Colored dashed lines in DAS indicate formation or decay of the specified detection component

Global Analysis: Mathematical tool to spectrally and temporally fitting 2DES data with n exponential decays and their amplitudes.

$$S(\lambda_{exc}, t_2, \lambda_{det}) = \sum_{i=1}^{n} A_i(\lambda_{exc}, \lambda_{det}) e^{-\frac{t_2}{\tau_i}}$$

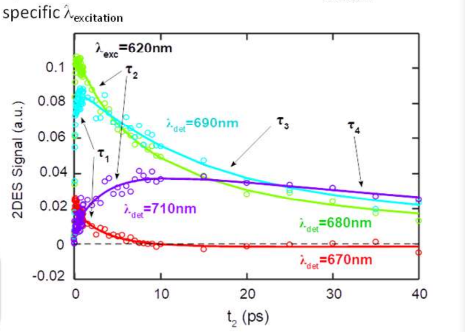
This calculation produce in output a collection of 2D maps A_i, called **Decay associated Spectra** (DAS) that show the Amplitude of each decay component τ_i for every $\lambda_{exc}/\lambda_{det}$ points [4].

Best fit: n =4 → Sequential four-level model

Legend: Formation Decay

330 fs: - decay at 670 nm and raise at 690 nm
3 ps: - decay at 680 nm and raise at 710 nm
10 ps: - decay at 690 nm
>40 ps: - decay at 700-730 nm

Dynamics extract from 2DES at different $\lambda_{detection}$ at a specific $\lambda_{excitation}$



Conclusion

Our Results point out the following deactivation Energy Transfer Pathways:

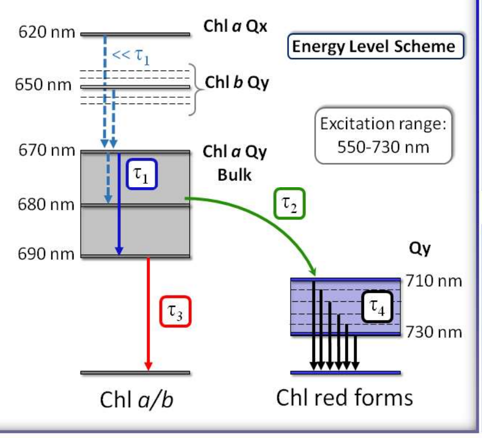
$\ll\tau_1$ Transitions from Short λ to Bulk Chl *a*

τ_1 → **330fs** Qy of Chl *a* intraband transition

τ_2 → **3ps** Energy transfer from Chl *a* Qy band to Qy Chl red forms

τ_3 → **10ps** Relaxation from the lowest energy level of Chl *a* Qy band

τ_4 → **>40ps** Decay of the Chl red forms Qy band



Acknowledgements

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Biophysics of Photosynthesis From molecules to the field

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