UNIVERSITY OF CAMBRIDGE

Intra-Protein Photodynamics of Photosystem II-Synthetic Hybrid Systems

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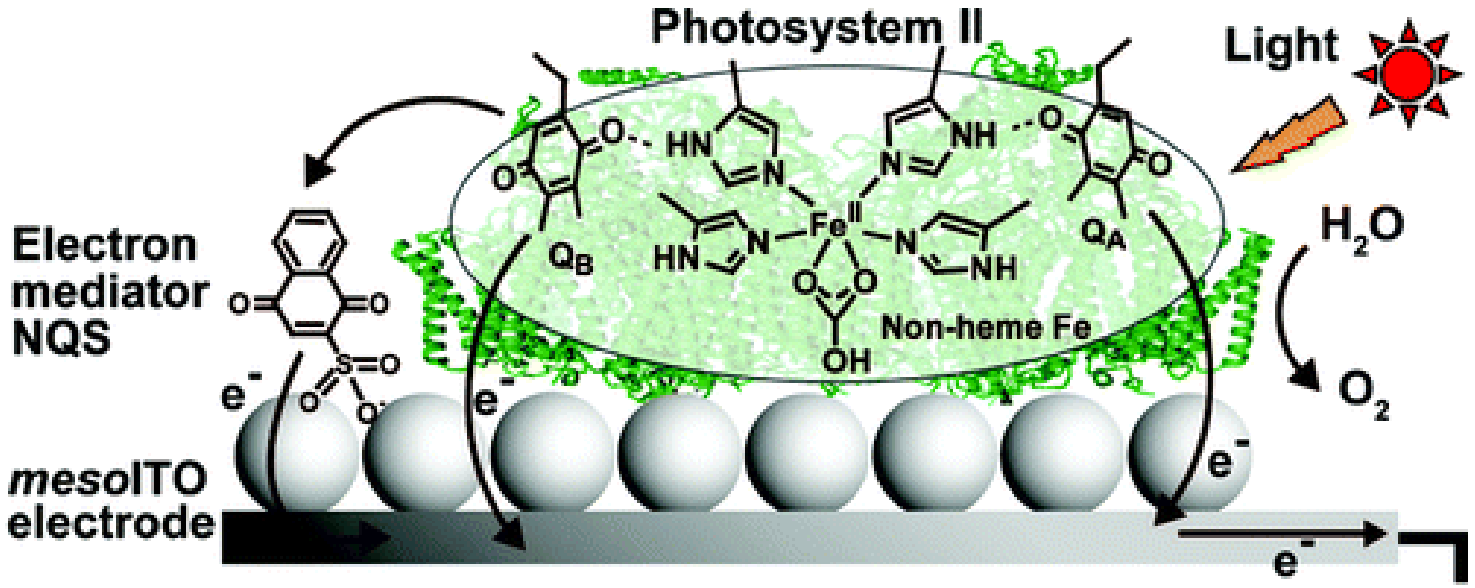
10th April 2014 (Day 2), COST Action TD1102, Istanbul, Turkey.

Contents

PSII-mesoITO: The Initial Idea

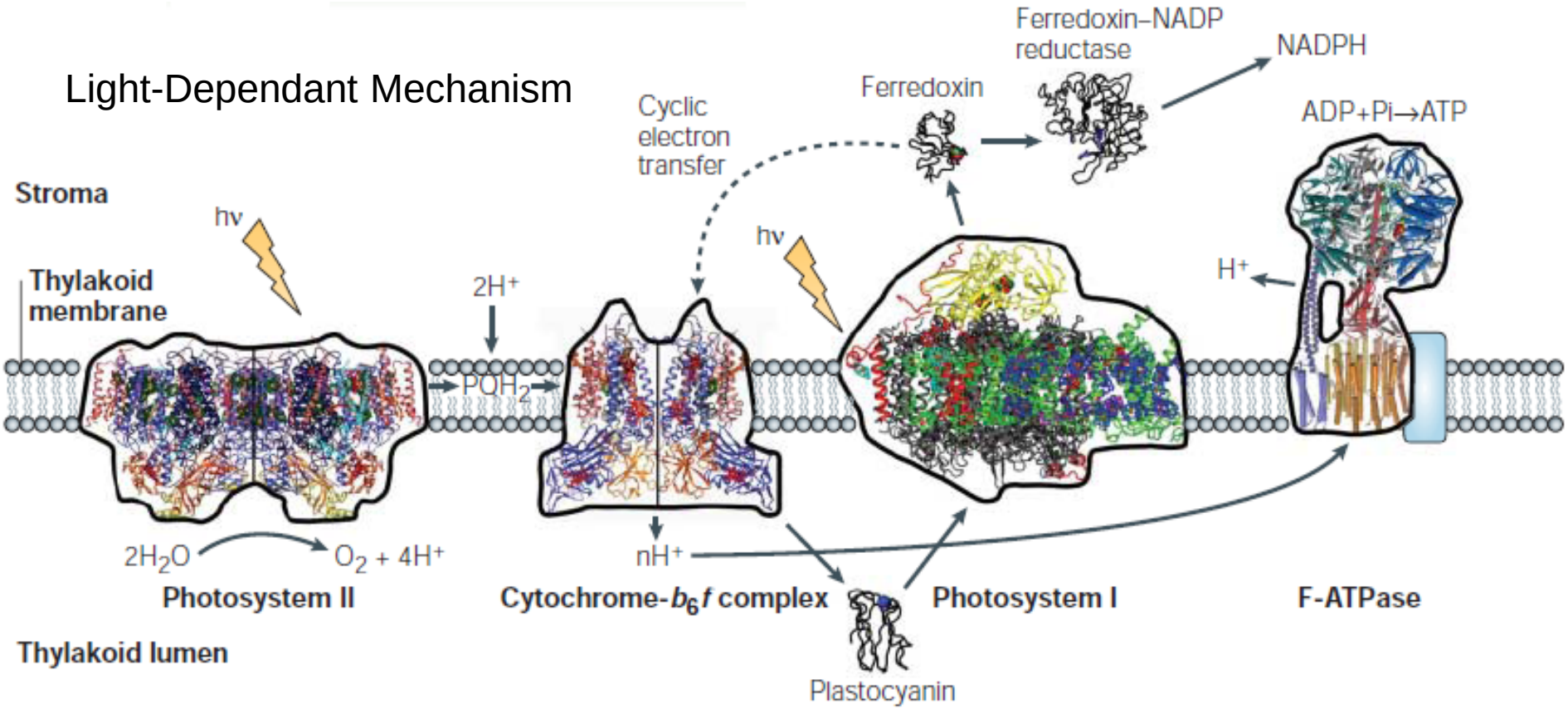


Kato. M *et.al.*, *Chem. Soc. Rev*, **2014**, DOI: 10.1039/C4CS00031E.
Kato. M *et.al*., *JACS*, **2013**, *135*, 10610-10613

- What is the rate/timescale of the interfacial electron transfer?
- Why does it even occur?
- What happened to the rest of the exciton and charge processes? Are they still the same or have they been altered?

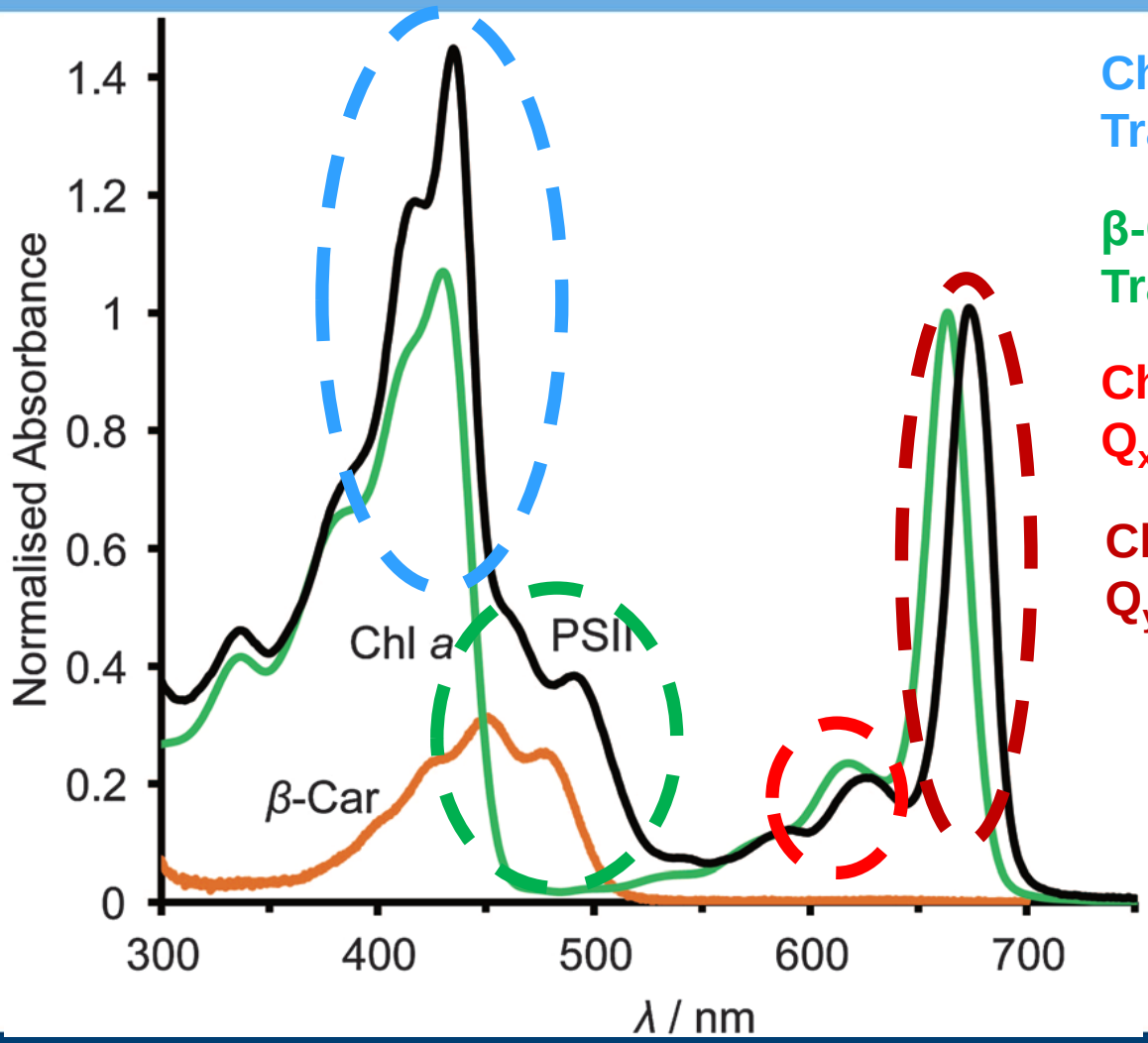
PSII: Function

Light-Dependant Mechanism



Nelson. N, *Nat. Rev. Mol. Cell. Bio*, **2004**, *5*, 1-12

PSII: Function



Chlorophyll Soret B Transitions

β-Carotene $S_0 – S_2$ Transition

Chlorophyll Q_x Transition

Chlorophyll Q_y Transition

Direction of Energy Transfer

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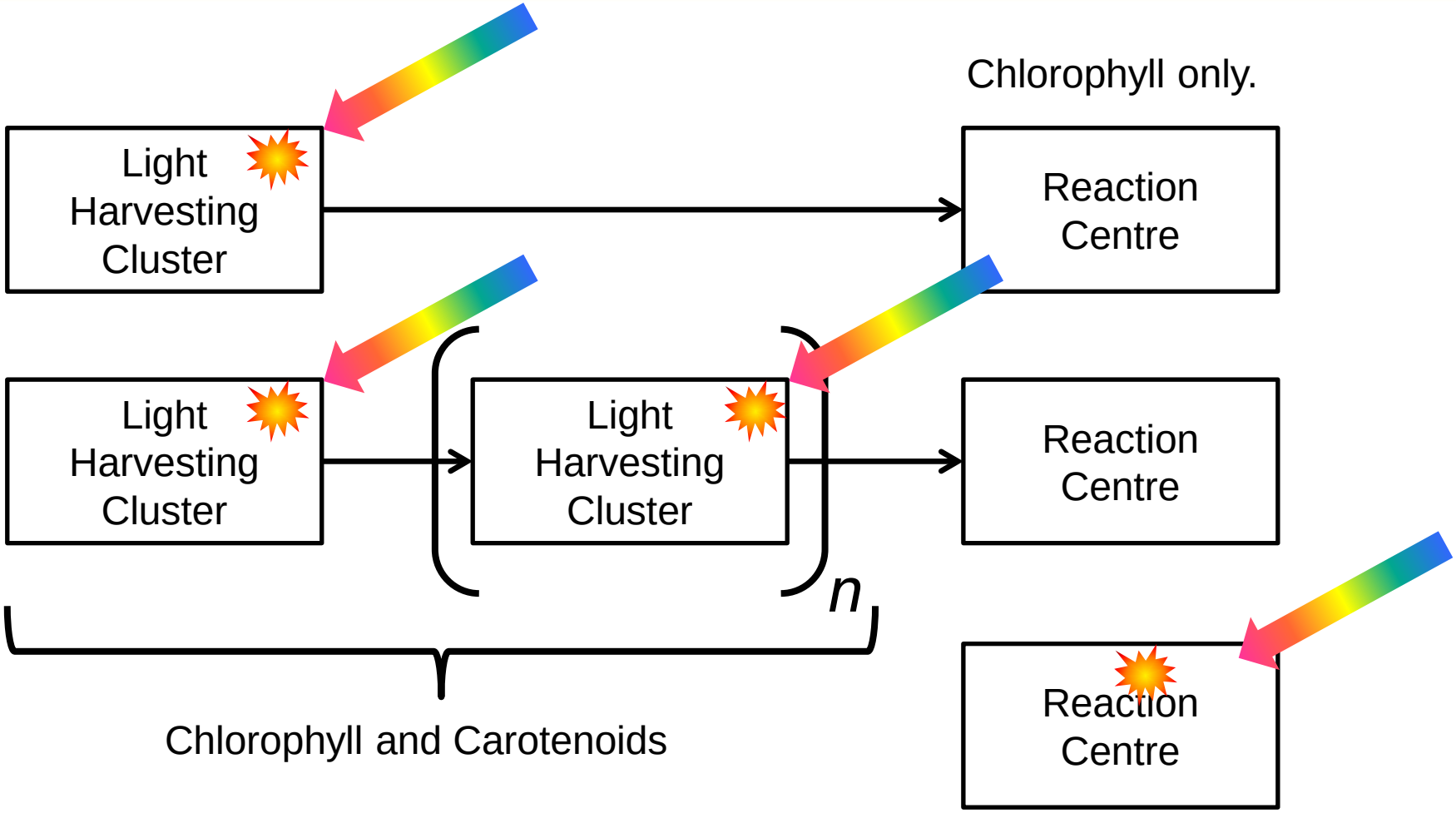
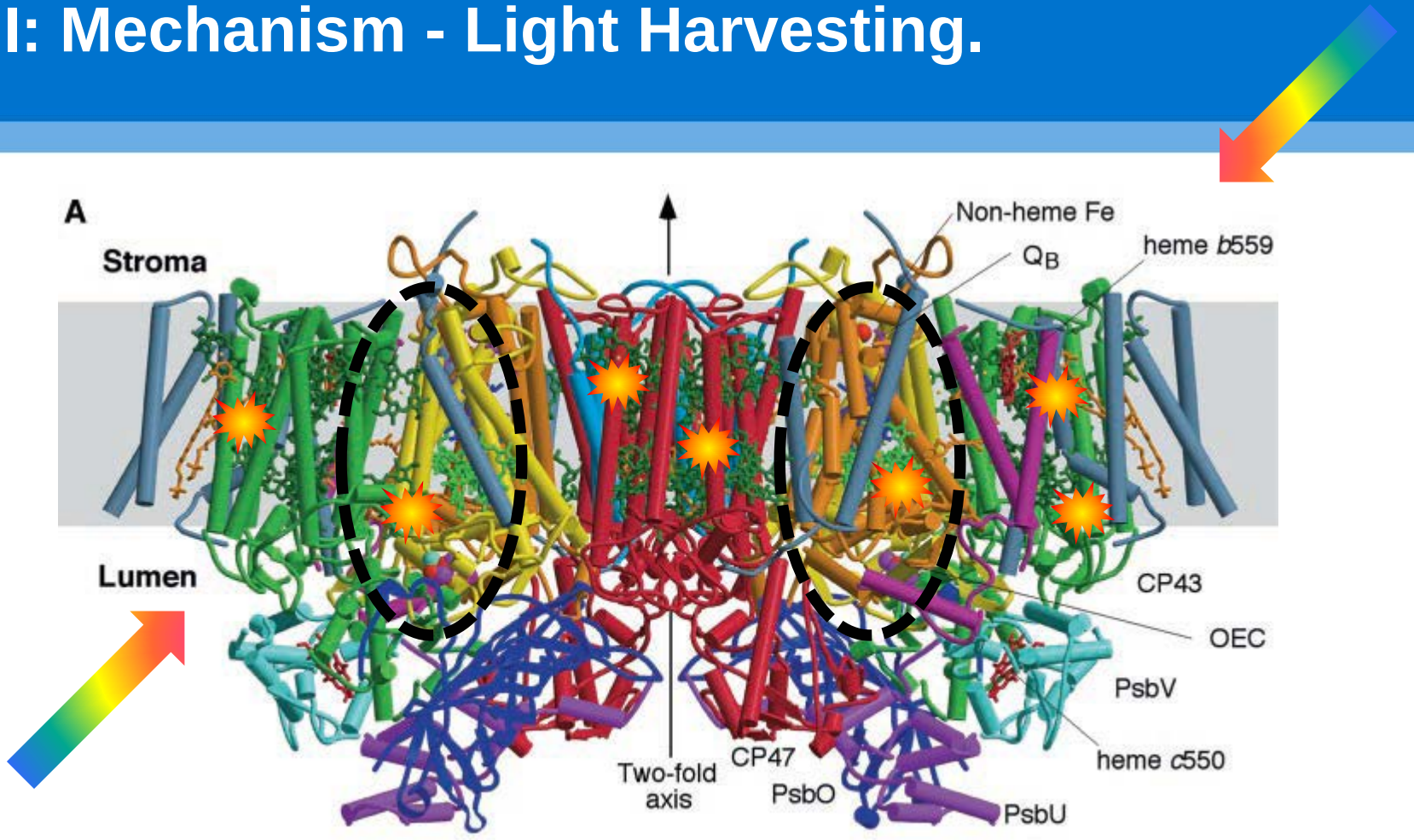
PSII: Mechanism - Light Harvesting.

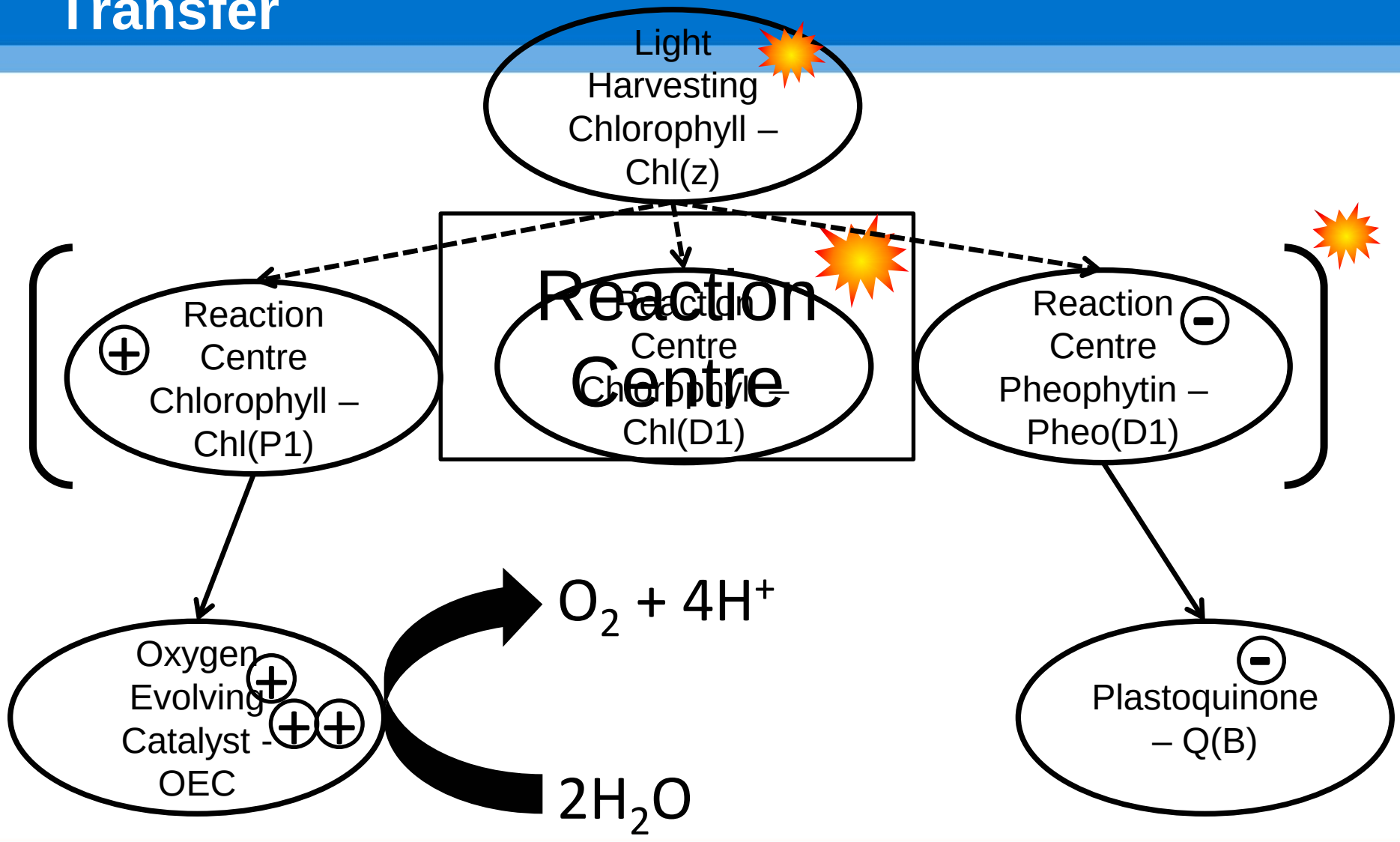


PSII: Mechanism - Light Harvesting.



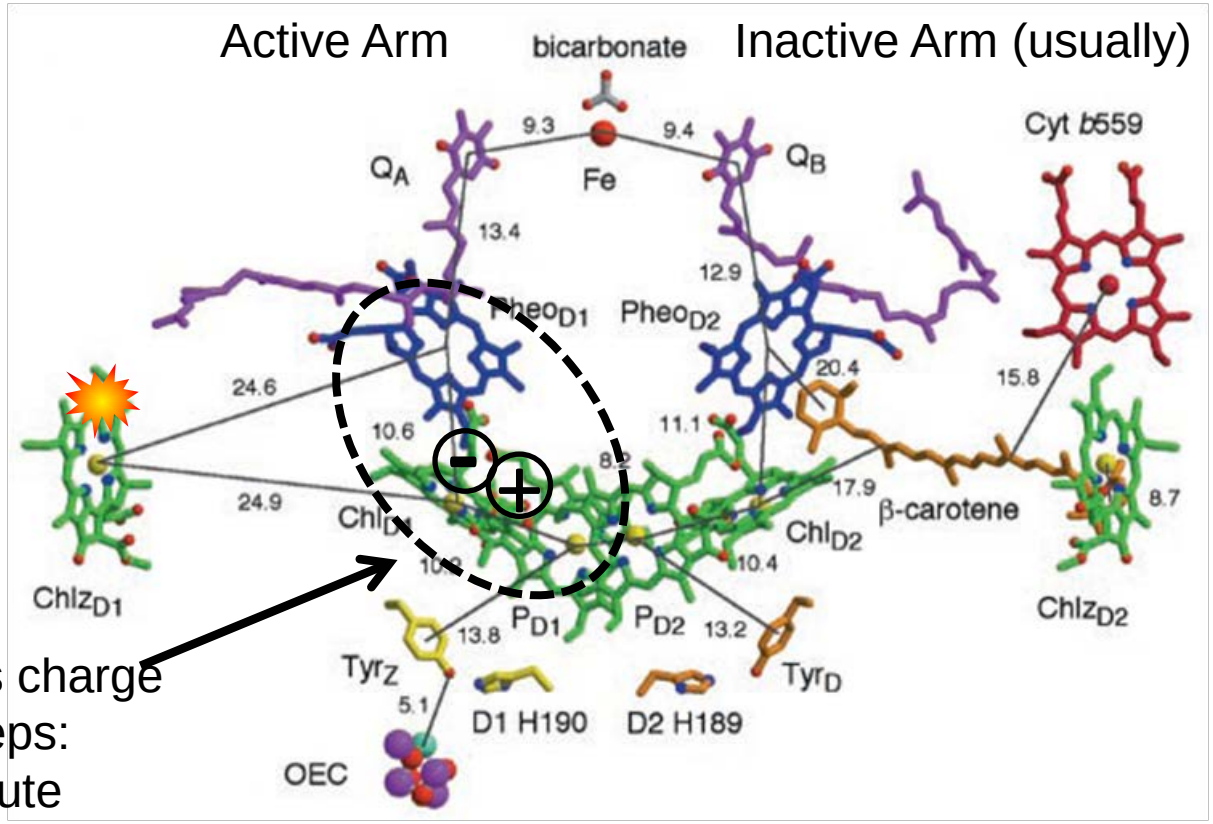
Ferreira, K. N, *Science* **2004,** *303,* 1831-1838.
Grondelle, R. V. *Phys. Chem. Chem. Phys* **2010**, *12*, 7352-7365

PSII: Mechanism - Charge Generation and Transfer



PSII: Mechanism - Charge Generation and Transfer

Last Energy Transfer Step



The fs – ps charge transfer steps: Still in dispute

Ferreira, K. N, *Science* **2004,** *303,* 1831-1838. Ahn, T. K, *Science* **2008**, *320*, 794-797. Cardona, T, *BBA-Bioenergetics* **2012**, *1817*, 26-43

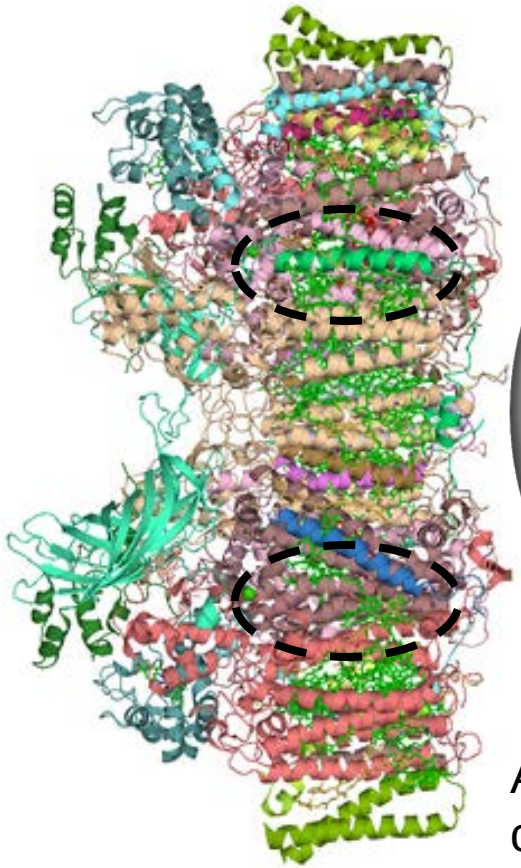
PhD Aims

1. **Perturbed intra-protein exciton and charge dynamics of PSII coupled to synthetic systems.** (*manuscript in preparation/to be submitted*).

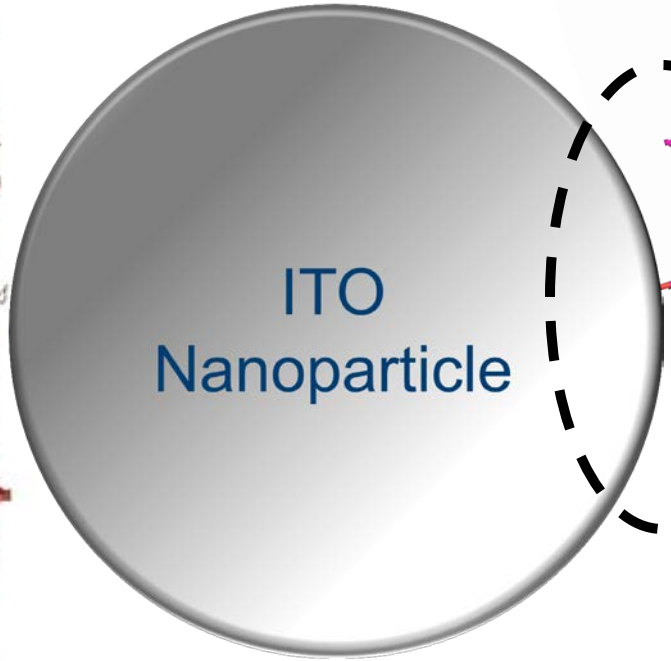
2. Interfacial electron transfer from PSII to synthetic systems. (*manuscript in preparation*).

3. New/alternative spectroscopic techniques and data analysis methods applied to PSII.

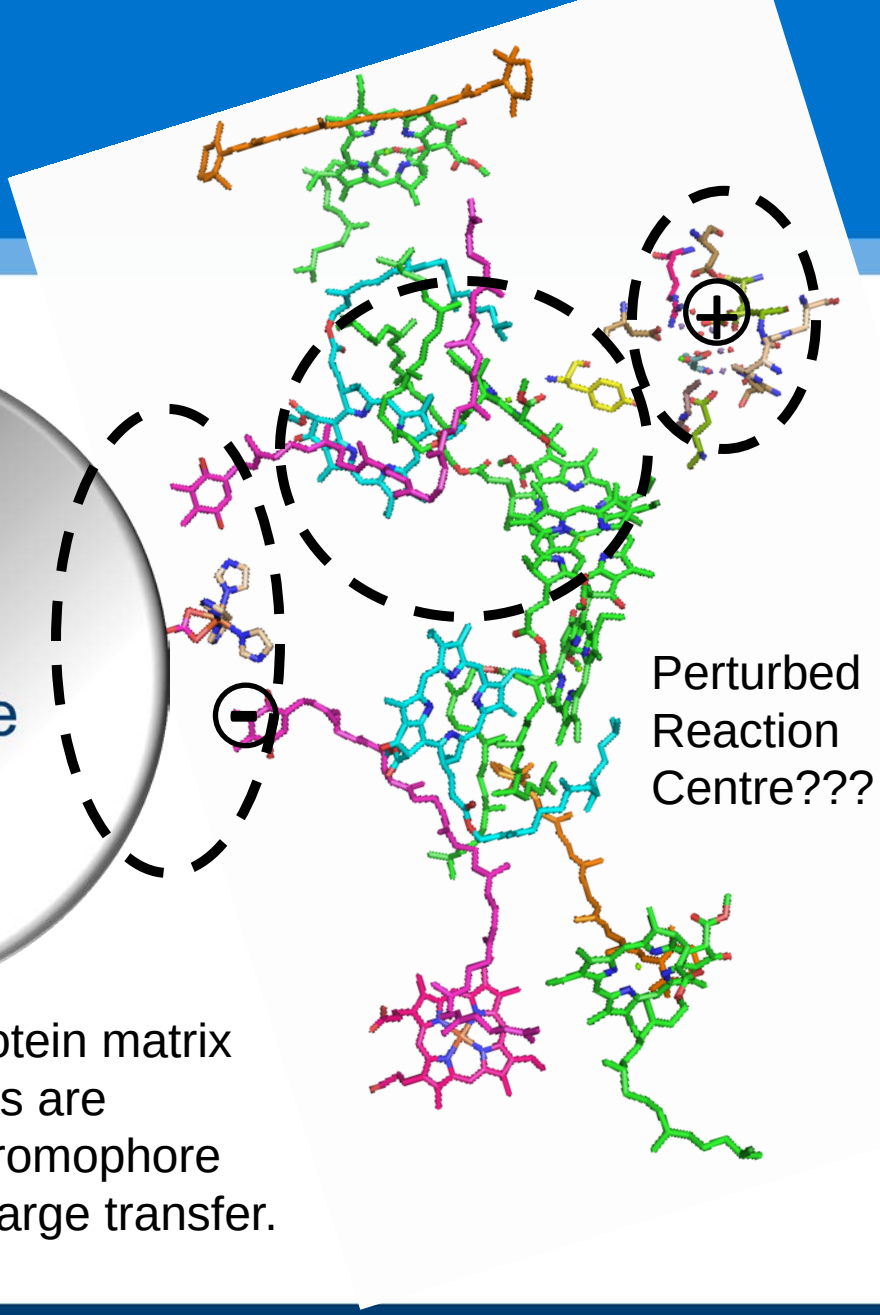
PhD Aims



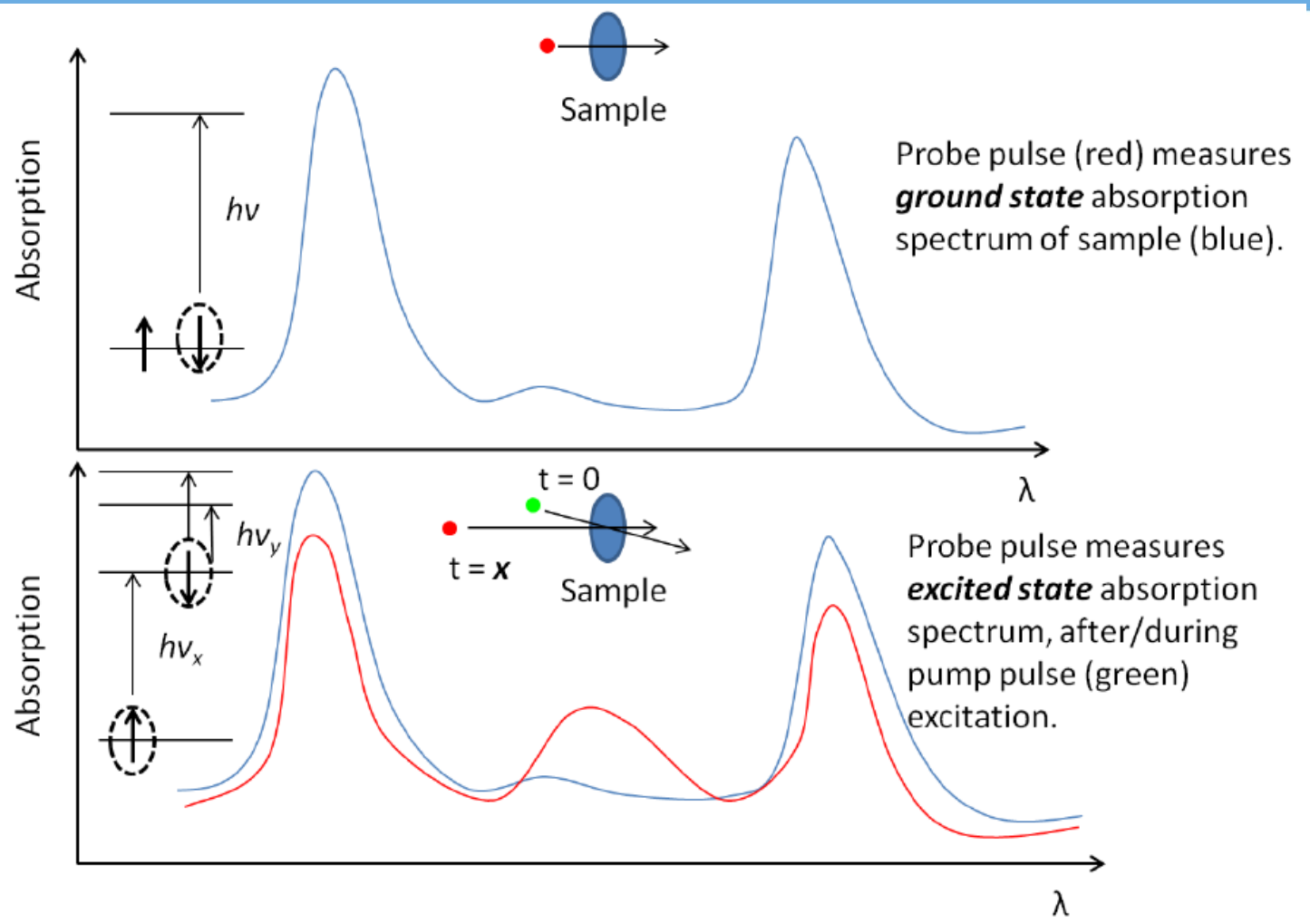
Are the antenna affected???



Adsorption-induced protein matrix conformational changes are predicted to reduce chromophore excitons and hinder charge transfer.

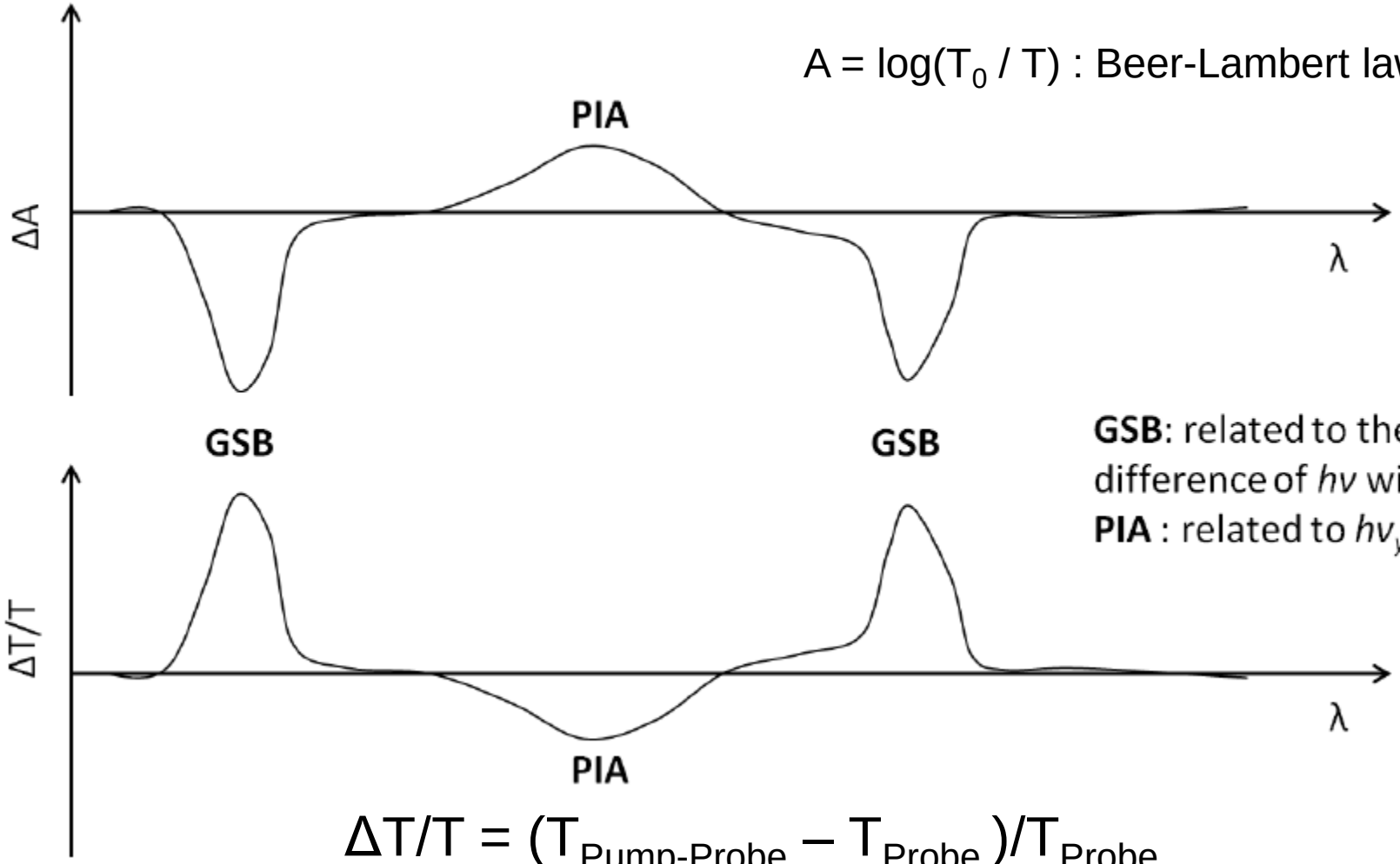


Transient Absorption Spectroscopy



Transient Absorption Spectroscopy

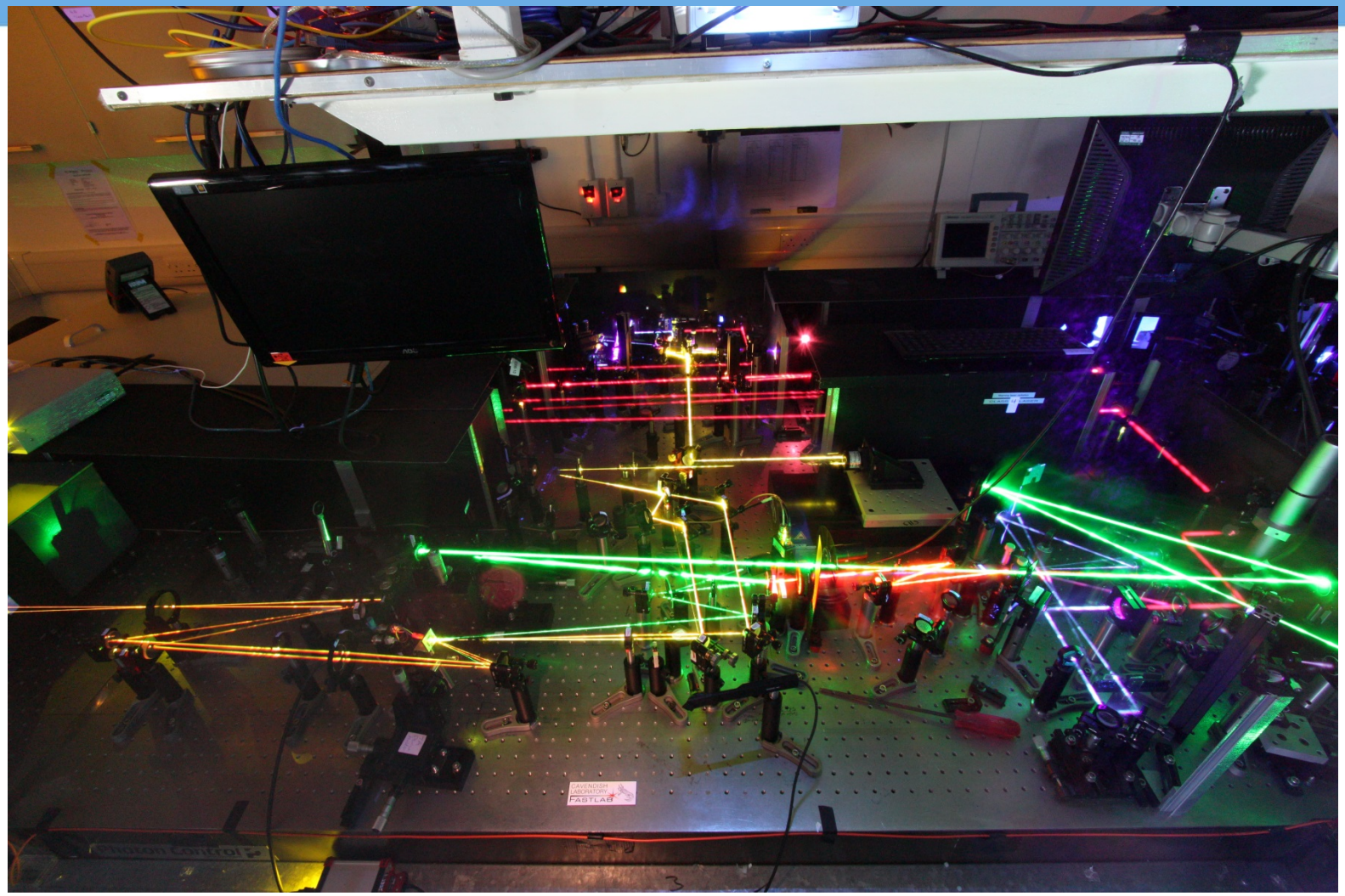
$A = \log(T_0 / T)$: Beer-Lambert law



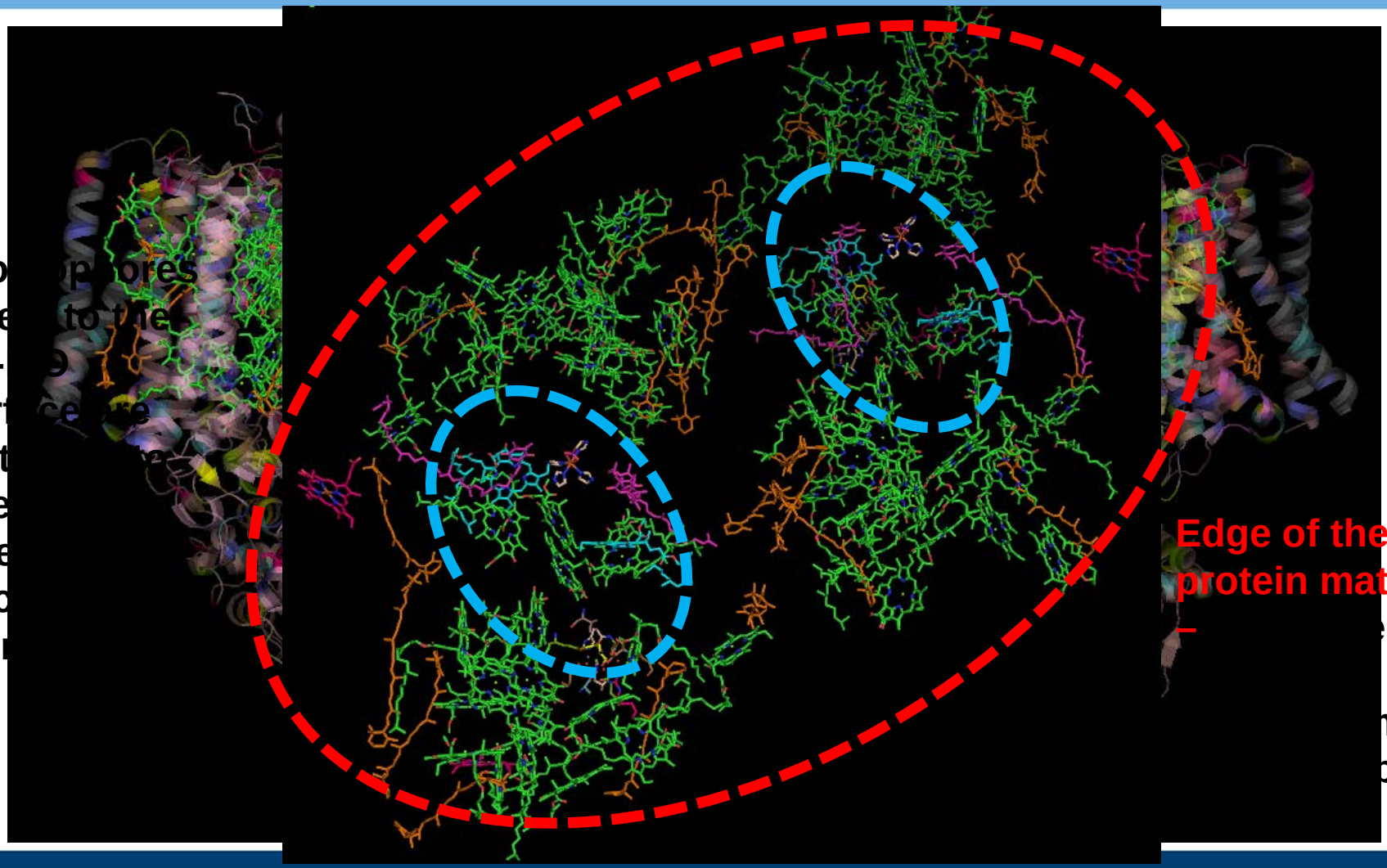
GSB: related to the difference of hv with hv_x
PIA : related to hv_y

$$\Delta T/T = (T_{Pump\text{-}Probe} - T_{Probe})/T_{Probe}$$

Transient Absorption Spectroscopy



Hypothesis



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Summary

- Aggregation of PSII to synthetic substrates may indeed induce altered photodynamics.
- These effects (if observable) are likely to be localized around the protein-substrate binding interface.
- PSII chlorophyll in the antenna (and likely close to the protein shell) seem to be affected the most, or almost exclusively.
- Increased non-radiative decay of the chlorophyll singlets due to the protein-substrate adsorption seems to be the end outcome.
- The reaction centre itself appears relatively well shielded.

The Chemists


The Physicists
Felix
Simon
Brian
Sebastian
Jenny (C)
Akshay

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- Friend Group
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Thank you for your attention!