2D ELECTRONIC SPECTROSCOPY

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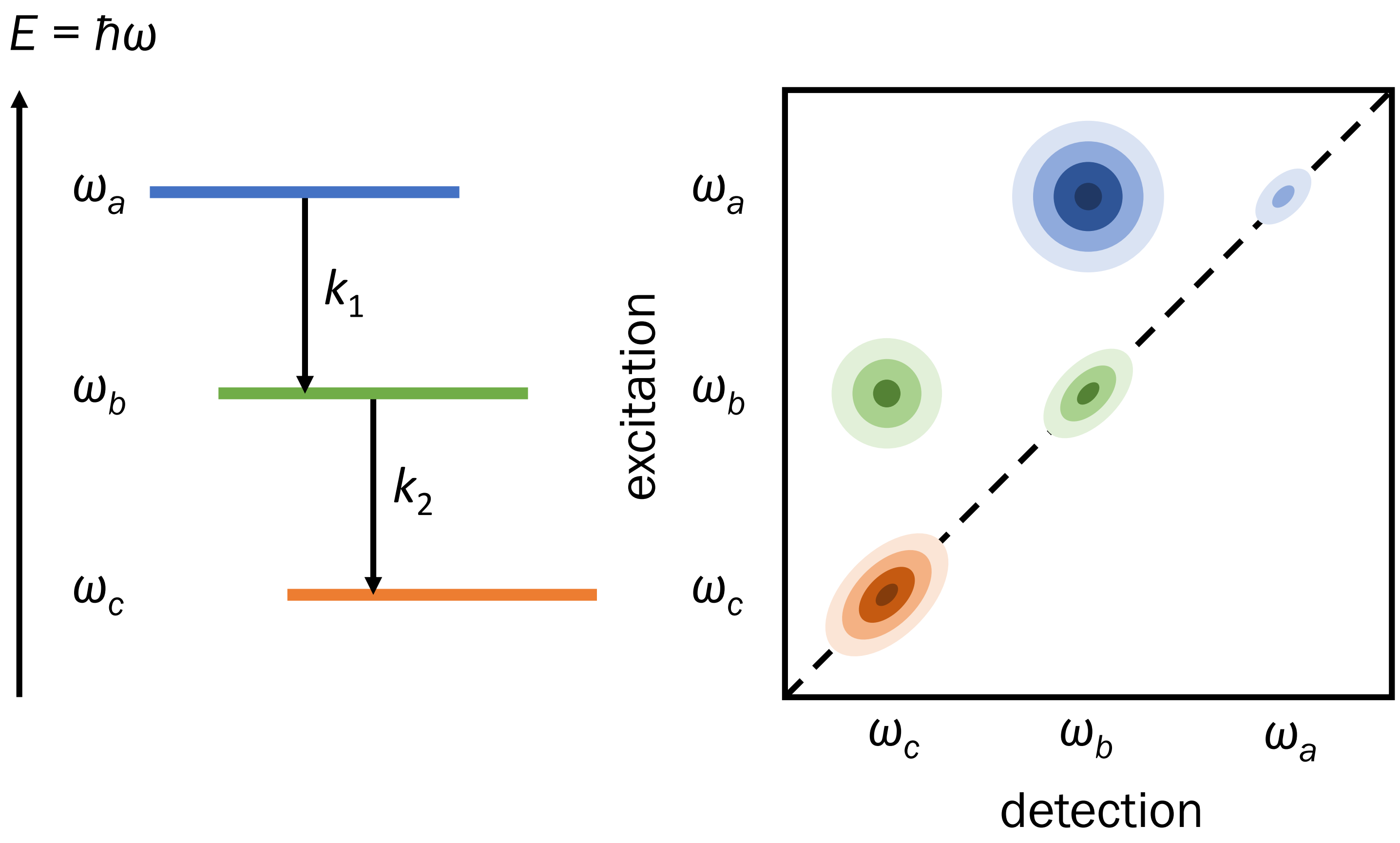
2D ELECTRONIC SPECTROSCOPY FUNDAMENTALS



Schematic 2D electronic spectrum of a coupled three-level system

2DES

- Measures the 3rd-order nonlinear optical response of the system
- Provides a time-dependent correlation map between two frequencies
- Contains all information about the system that can be gathered by any other type of 3rd-order spectroscopy:
- Electronic excited states
- Homogeneous and inhomogeneous linewidths
- Electronic couplings and coherences
- Excitation dynamics and pathways

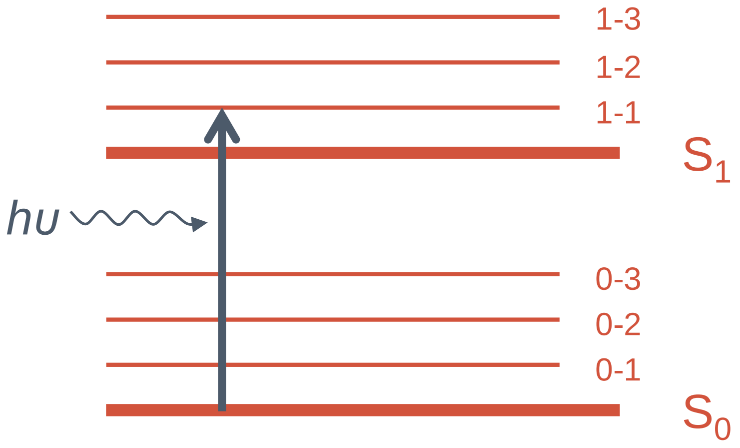
2D ELECTRONIC SPECTROSCOPY - OUTLINE

1. **Basic concepts**
   - Electronic transitions and spectral lines
   - Homogeneous and inhomogenous broadening
   - Molecular interactions and energy transfer
   - Quantum Coherence
   - Molecular excitons
   - Time-resolved spectroscopy
   - The double resonance experiment
   - Fourier transform 2DES

2. **Technical implementations**
   - Boxcars vs pump-probe geometry
   - Phase matching and phase cycling
   - Example experimental setups

3. **Application in photosynthesis**
   - Basics of photosynthetic light harvesting
   - Energy transfer in FMO
   - Energy transfer in LHCII

MOLECULAR ENERGY STATES AND TRANSITIONS



Eigenstates – solutions of the time-independent Schrödinger equation

$$E\Psi = \hat{H}\Psi$$

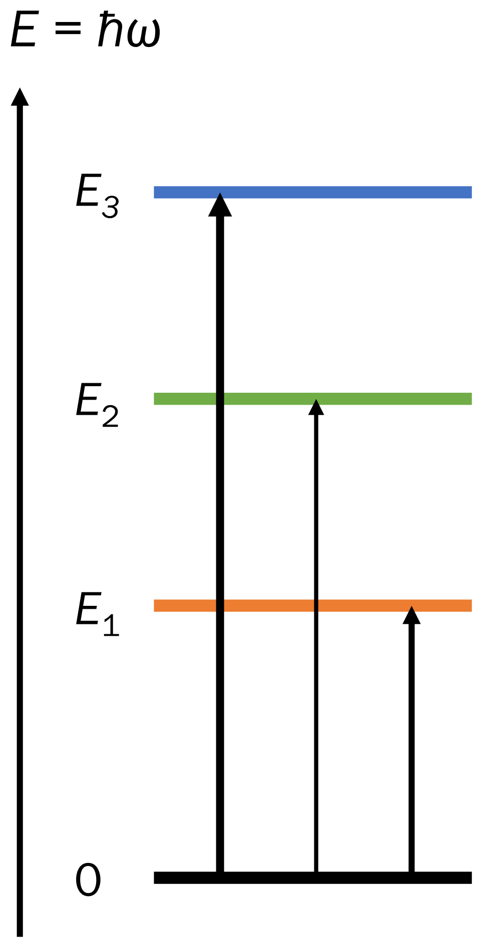
Transition dipole moment

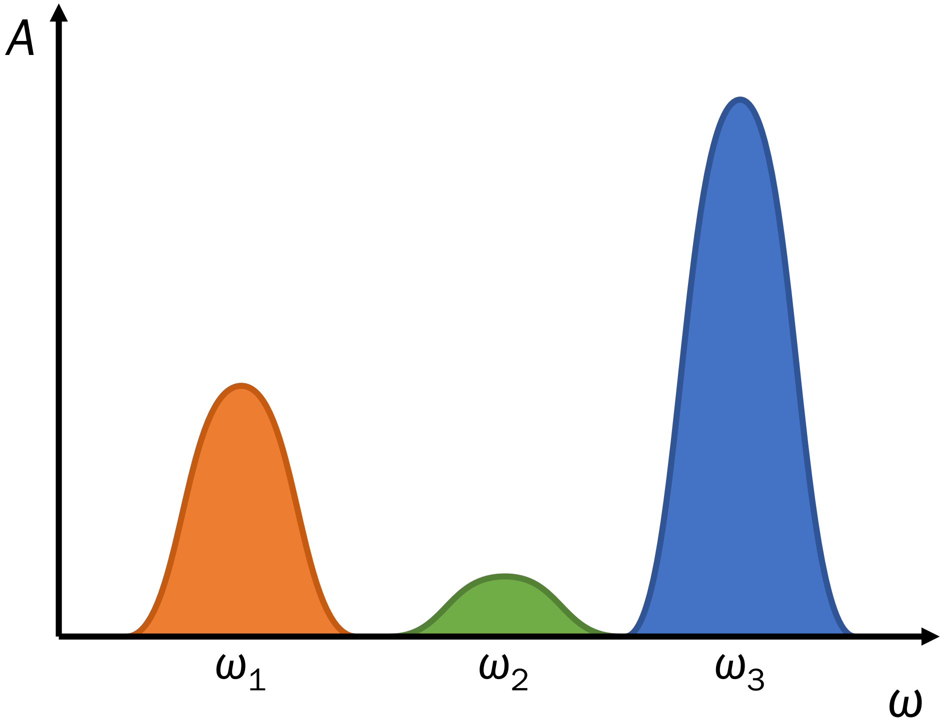
$$\boldsymbol{\mu} = \langle \Psi_0 | \boldsymbol{\mu} | \Psi_1 \rangle = q \int \Psi_0^*(\mathbf{r})\, \boldsymbol{r}\, \Psi_1(\mathbf{r})\, \mathrm{d}^3\mathbf{r}$$

Transition probability (Fermi's Golden Rule)

$$E_0^2 \cdot \left| \hat{\mathbf{E}} \cdot \langle \Psi_0 | \boldsymbol{\mu} | \Psi_1 \rangle \right|^2 = |\mathbf{E_0}|^2 \cdot |\boldsymbol{\mu}|^2 \cdot \cos^2(\hat{\mathbf{E}} \cdot \hat{\boldsymbol{\mu}})$$

ABSORPTION SPECTRA





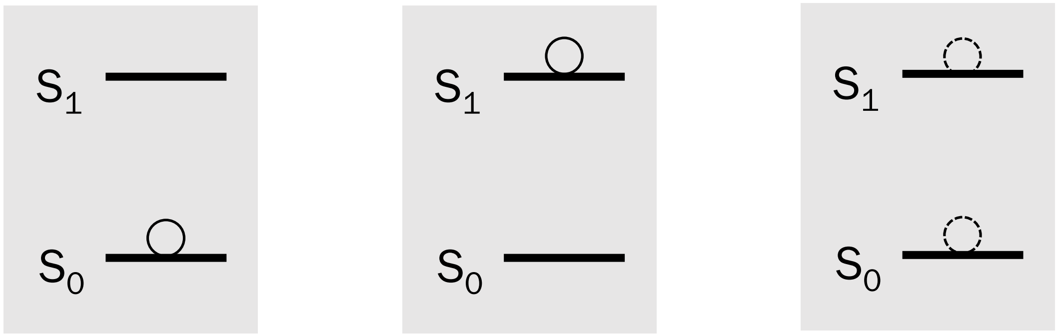
- Absorption bands correspond to energy eigenstates
- The intensity of the absorption band is proportional to the dipole strength (and chromophore concentration)

$$D = \mu^2$$

- The width of the band is controlled by homogeneous and inhomogeneous broadening effects

QUANTUM COHERENCE

Ground state | Excited state | Coherence state



Ψ_0 | Ψ_1 | Ψ_{01}

Density matrix $\begin{vmatrix} 1 & 0 \\ 0 & 0 \end{vmatrix}$ $\begin{vmatrix} 0 & 0 \\ 0 & 1 \end{vmatrix}$ $\begin{vmatrix} 1/2 & -i/2 \\ i/2 & 1/2 \end{vmatrix}$

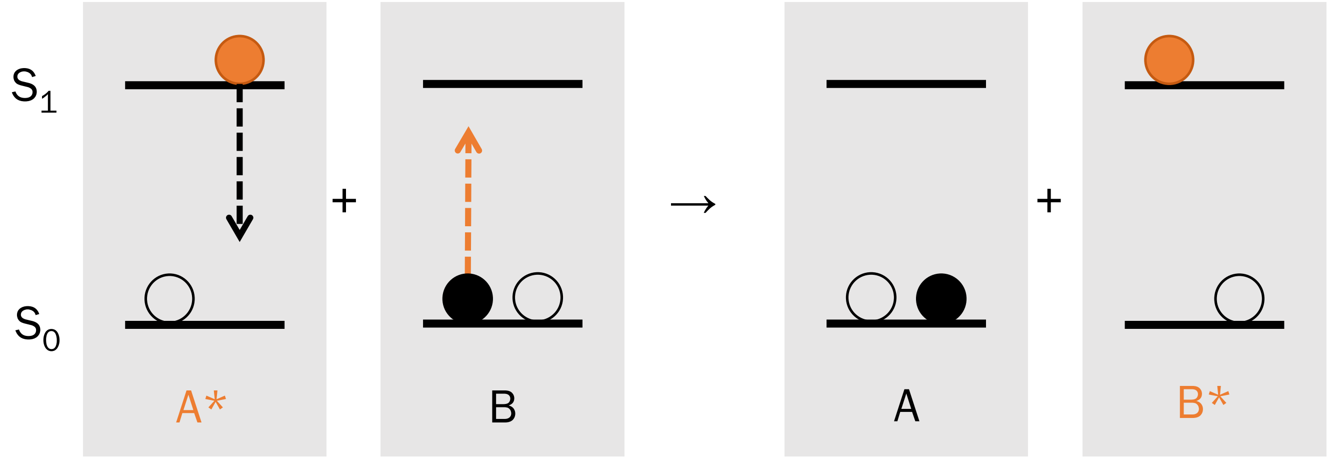
Coherent superposition of states

$$\Psi_{01} = c_0\Psi_0 + c_1\Psi_1 =$$
$$= c_0\psi_0 e^{-iE_0t/\hbar} + c_1\psi_1 e^{-iE_1t/\hbar}$$

Oscillation frequency

$$\omega_{01} = (E_1 - E_0)/\hbar$$

EXCITATION ENERGY TRANSFER



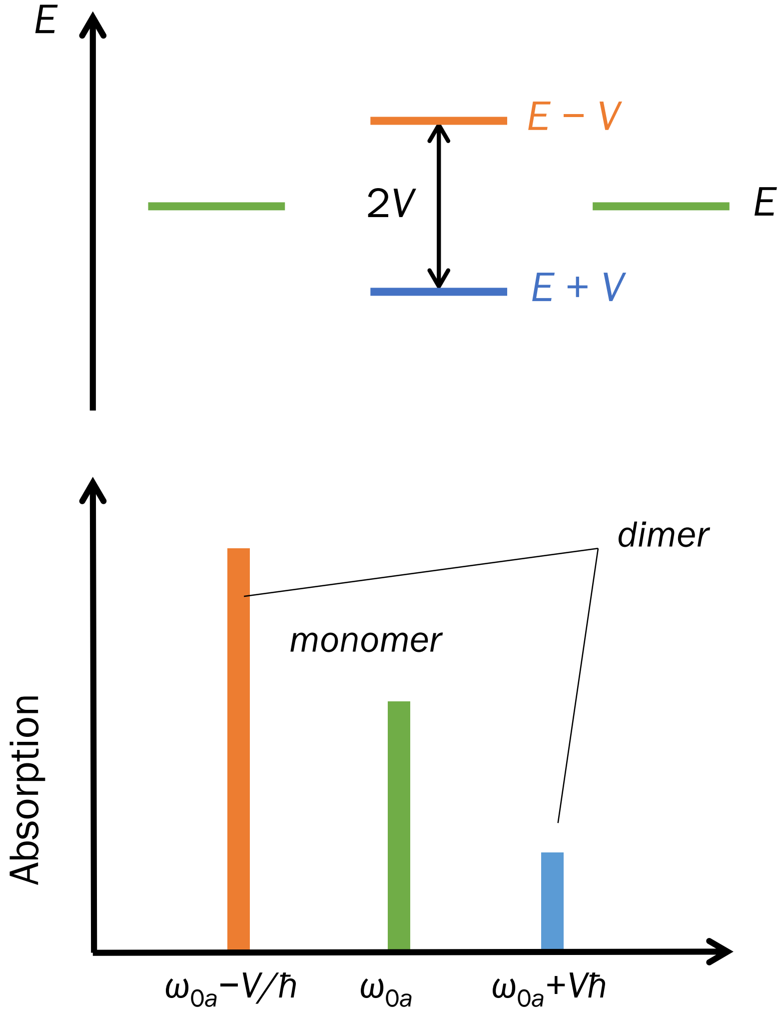
Förster resonance energy transfer

$$k_{AB} = \frac{9\kappa^2 c^4}{8\pi\tau_{A^*} n^4 R^6} \int F_A(\omega)\sigma_B(\omega)\frac{\mathrm{d}\omega}{\omega^4}$$

Typical energy transfer times

10^{-14}–10^{-9} s

THE EXCITONIC DIMER



Exciton (Frenkel) Hamiltonian

$$H = H_1 + H_2 + V$$

$$V = \frac{1}{4\pi\varepsilon_0 r^3}\left(\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 - 3(\boldsymbol{\mu}_1 \cdot \hat{\mathbf{r}})(\boldsymbol{\mu}_2 \cdot \hat{\mathbf{r}})\right)$$

$$(H_1 + H_2 + V)\Psi_\alpha = E_\alpha \Psi_\alpha$$

$$\mathbf{H} = \begin{vmatrix} \langle\Psi_1|H|\Psi_1\rangle & \langle\Psi_1|H|\Psi_2\rangle \\ \langle\Psi_2|H|\Psi_1\rangle & \langle\Psi_2|H|\Psi_2\rangle \end{vmatrix} = \begin{vmatrix} E_1 & V \\ V & E_2 \end{vmatrix}$$

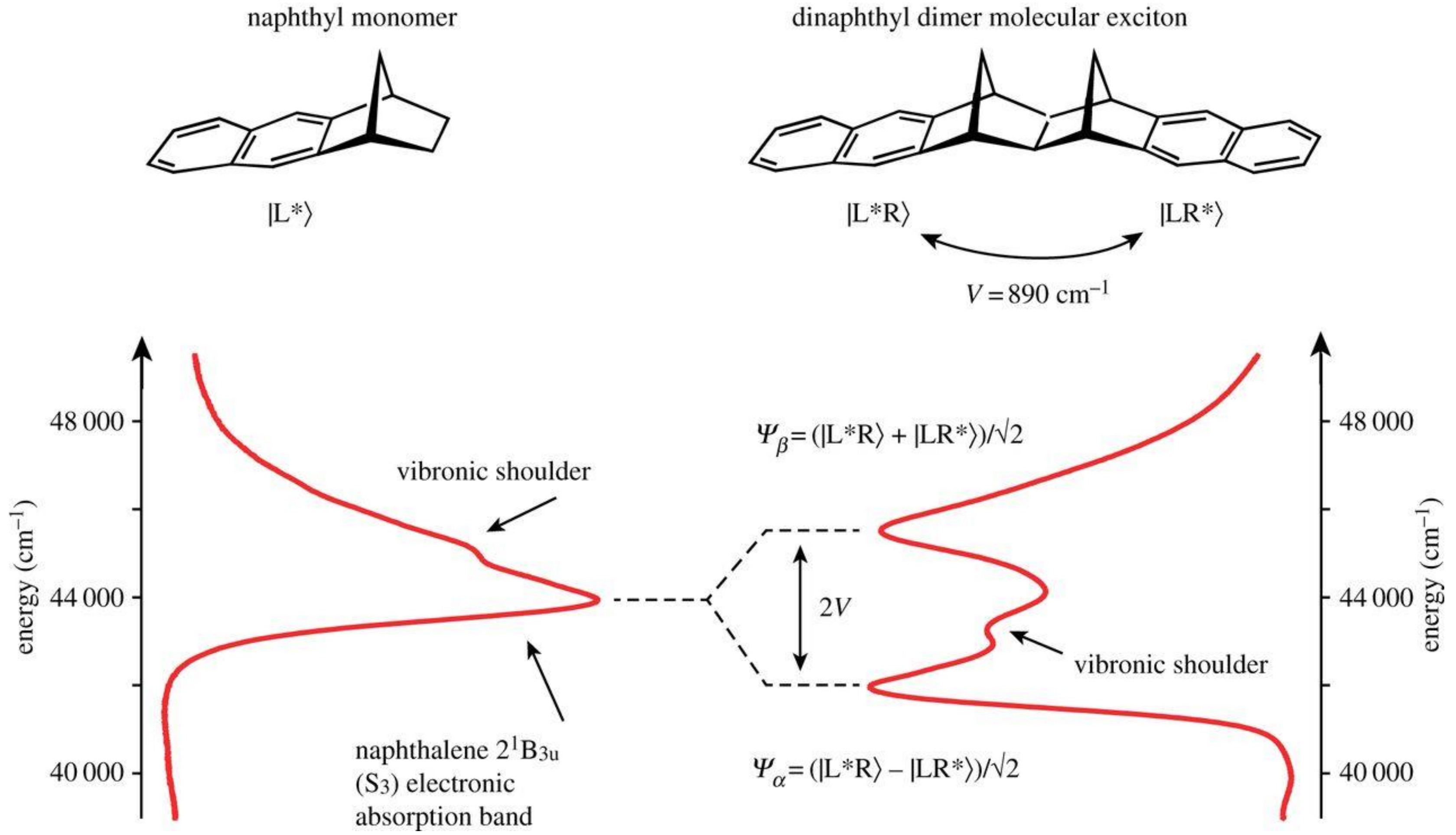
Solution – exciton states

$$E_\alpha = E \pm V$$

$$\Psi_\alpha = \frac{1}{\sqrt{2}}(\Psi_1 \pm \Psi_2)$$

$$\boldsymbol{\mu}_\alpha = \frac{1}{\sqrt{2}}(\boldsymbol{\mu}_1 \pm \boldsymbol{\mu}_2)$$

MOLECULAR EXCITONS



Fassioli *et al.* (2014) *JRS Interface*

INCOHERENT VS. COHERENT TRANSFER

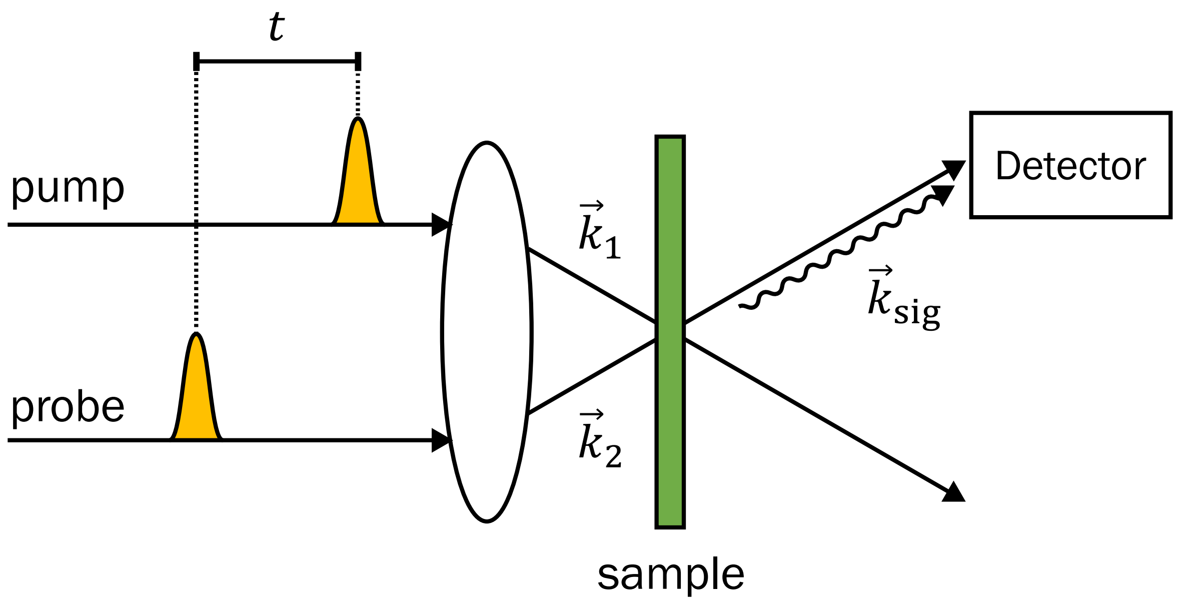
Weak coupling limit

- Weak chromophore interaction
- Localized excited states
- Vibrational relaxation is faster than energy transfer
- Incoherent hopping of excitations
- Rate of transfer depends on the the square of the dipole-dipole interaction
- Förster theory

Strong coupling limit

- Strong chromophore interaction
- Delocalized exciton states
- Energy transfer occurs before vibrational relaxation
- Wave-like excitation motions
- Rate of transfer depends on the quantum dipole-dipole interaction term
- Redfield theory

PUMP-PROBE SPECTROSCOPY

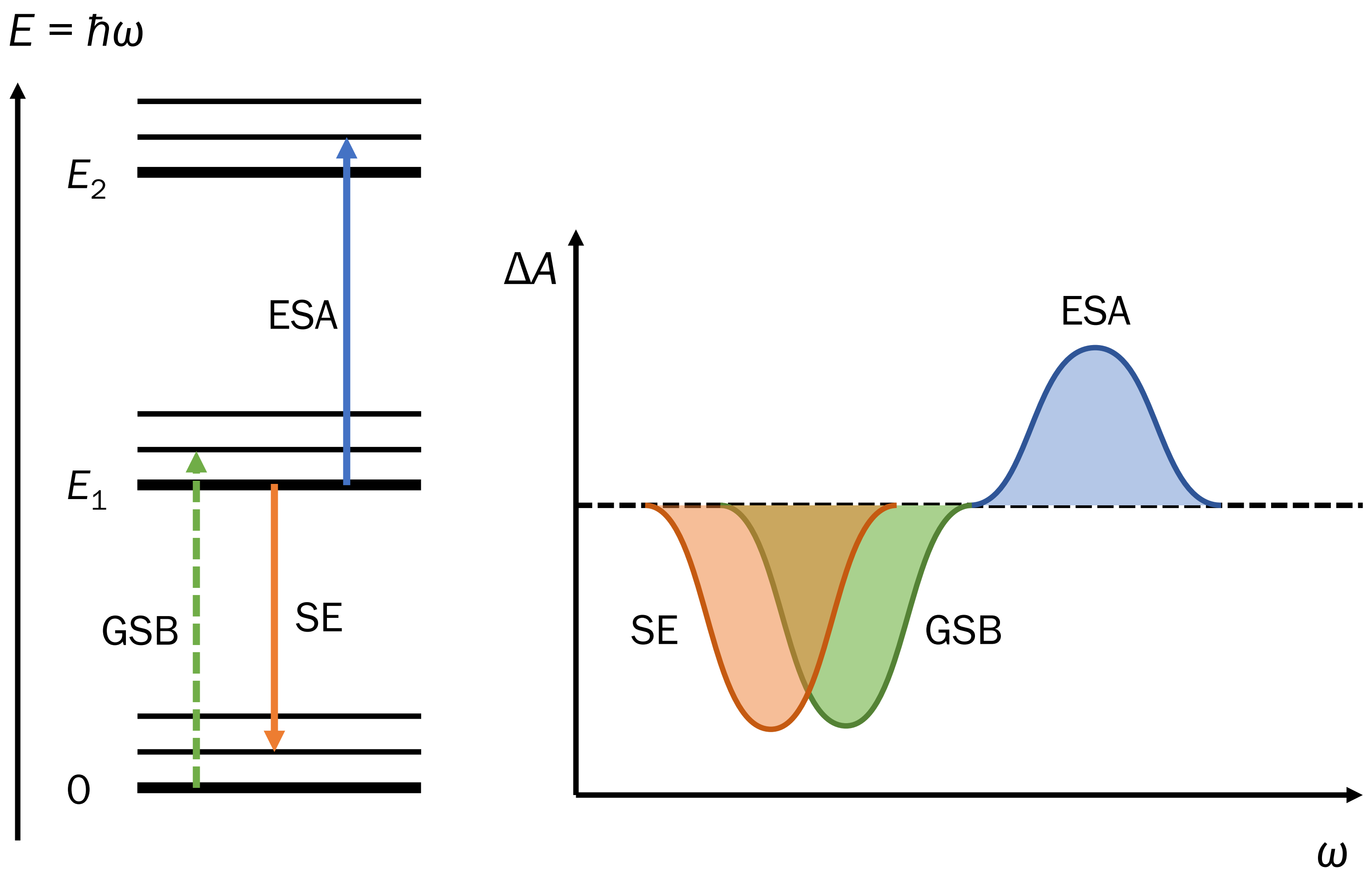


Differential absorption:
$\Delta A(t) = A_{+pump} - A_{-pump}$

- 'Pump' pulse creates excited states ($GS \rightarrow S_1$)
- A subsequent 'probe' pulse ($S_1 \rightarrow S_n$) measures the changes induced by the pump
- The temporal evolution is followed by scanning over the time between pump and probe
- Temporal resolution is only limited by the pulse duration
- 3rd order nonlinear spectroscopy
- Phase matching direction

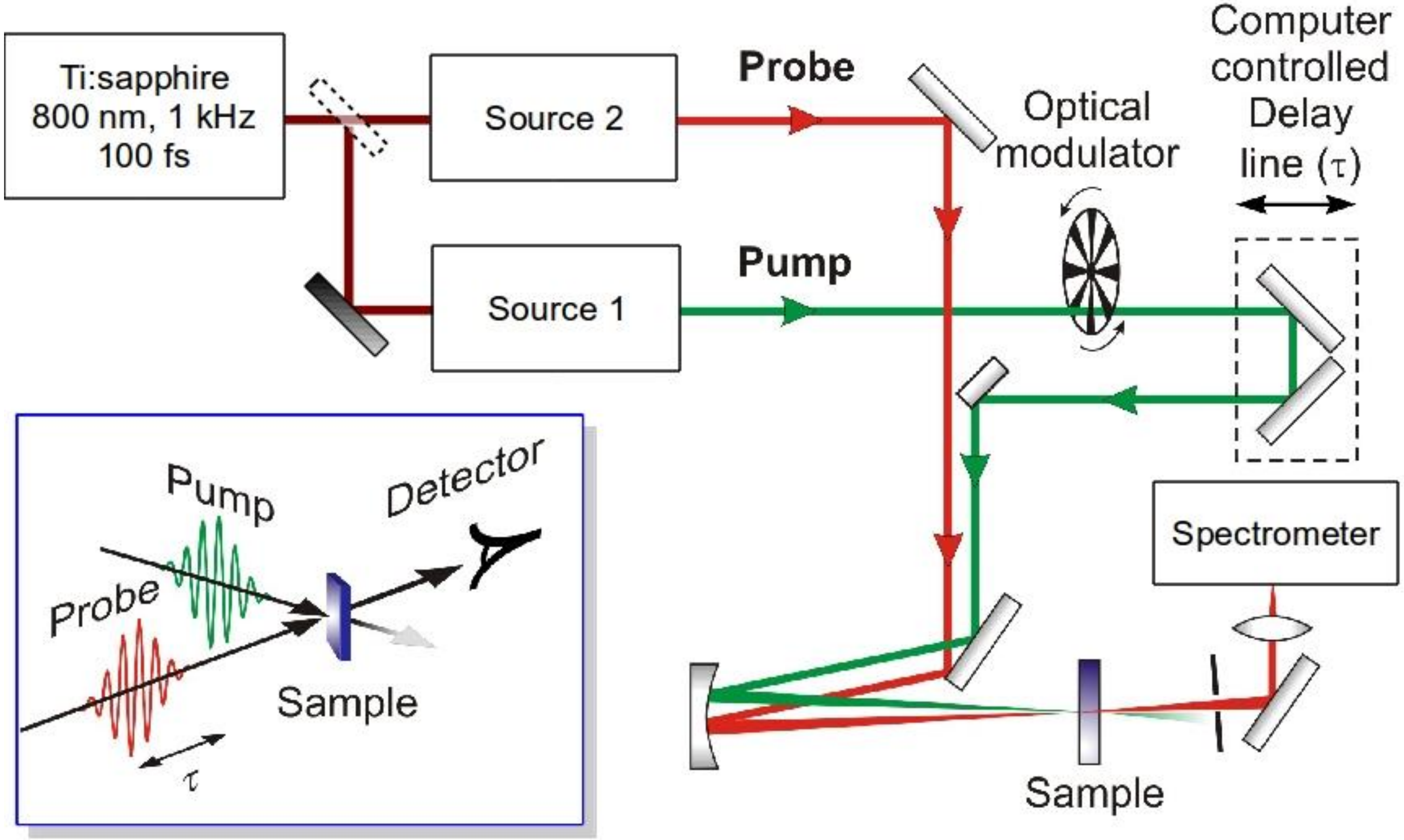
$$k_{sig} = k_1 - k_1 + k_2$$

TRANSIENT ABSORPTION SPECTRA

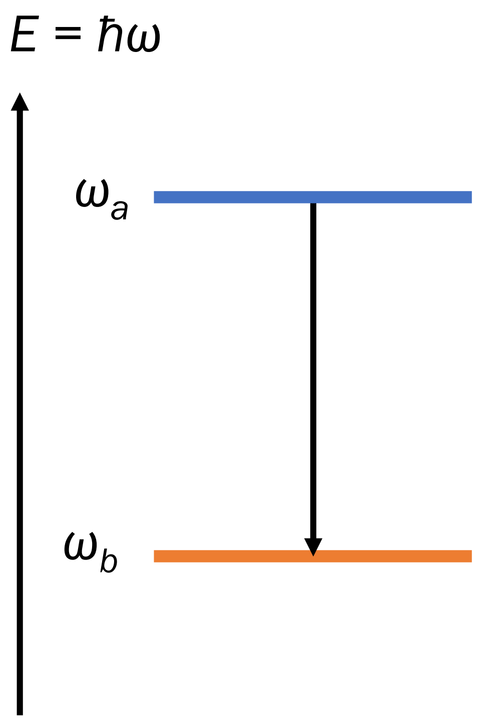


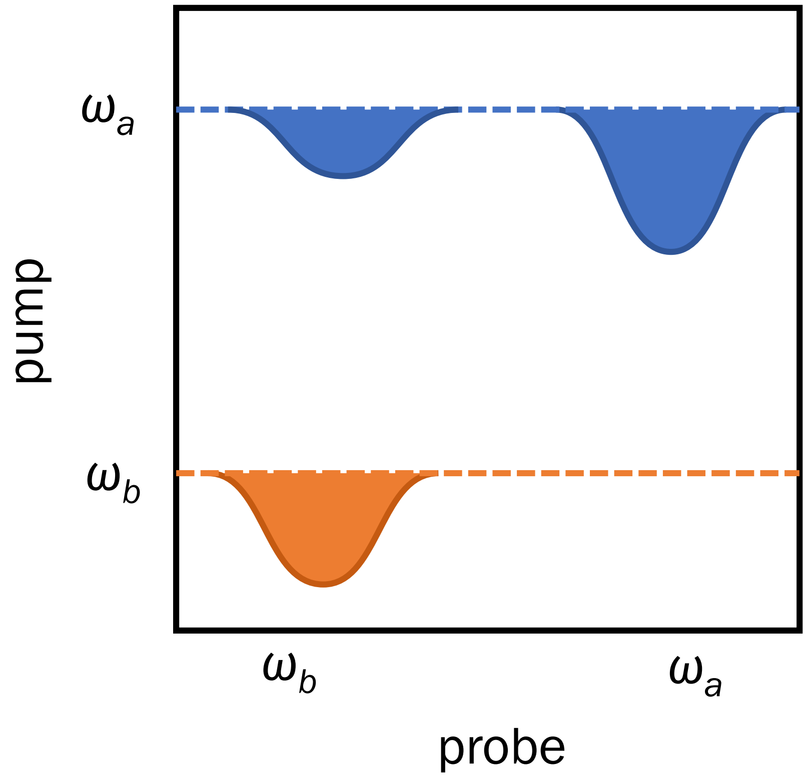
- GSB - ground-state bleaching
- SE - stimulated emission
- ESA - excited-state absorption

EXPERIMENTAL SETUP FOR PUMP-PROBE SPECTROSCOPY



"POOR-MAN" 2D SPECTROSCOPY – DOUBLE RESONANCE





Double resonance experiment (stacked pump-probe spectra)

- Narrowband pump – broadband probe
- The experiment is repeated with varying the pump wavelengths
- The spectra are stacked together to obtain a quasi-2D spectrum

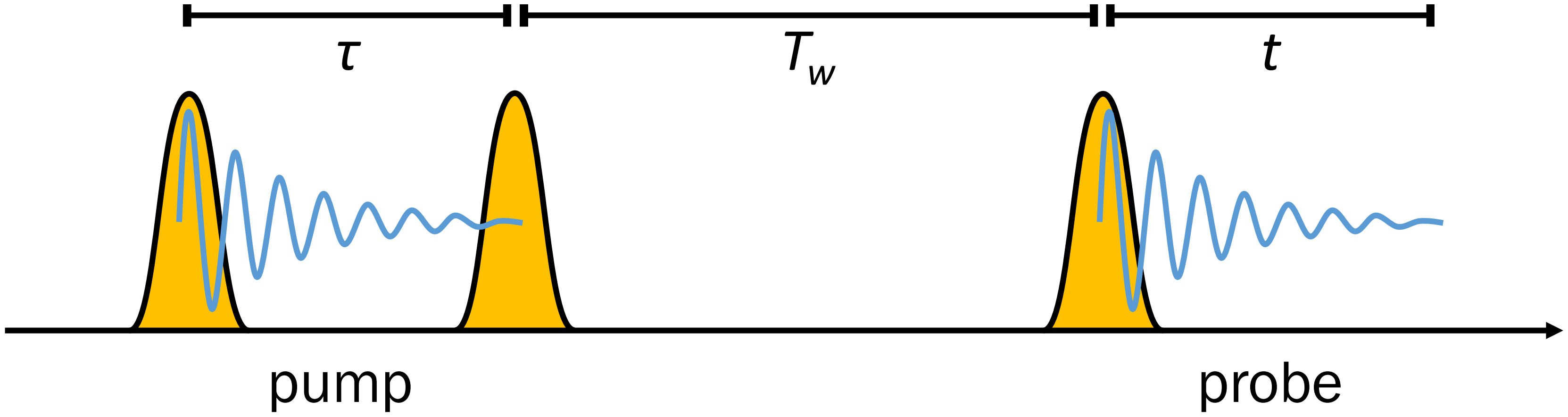
Problems

- Laborious and time consuming (repeated experiments with different excitations)
- Transform limit imposes a trade-off between time and spectral resolution

Solution

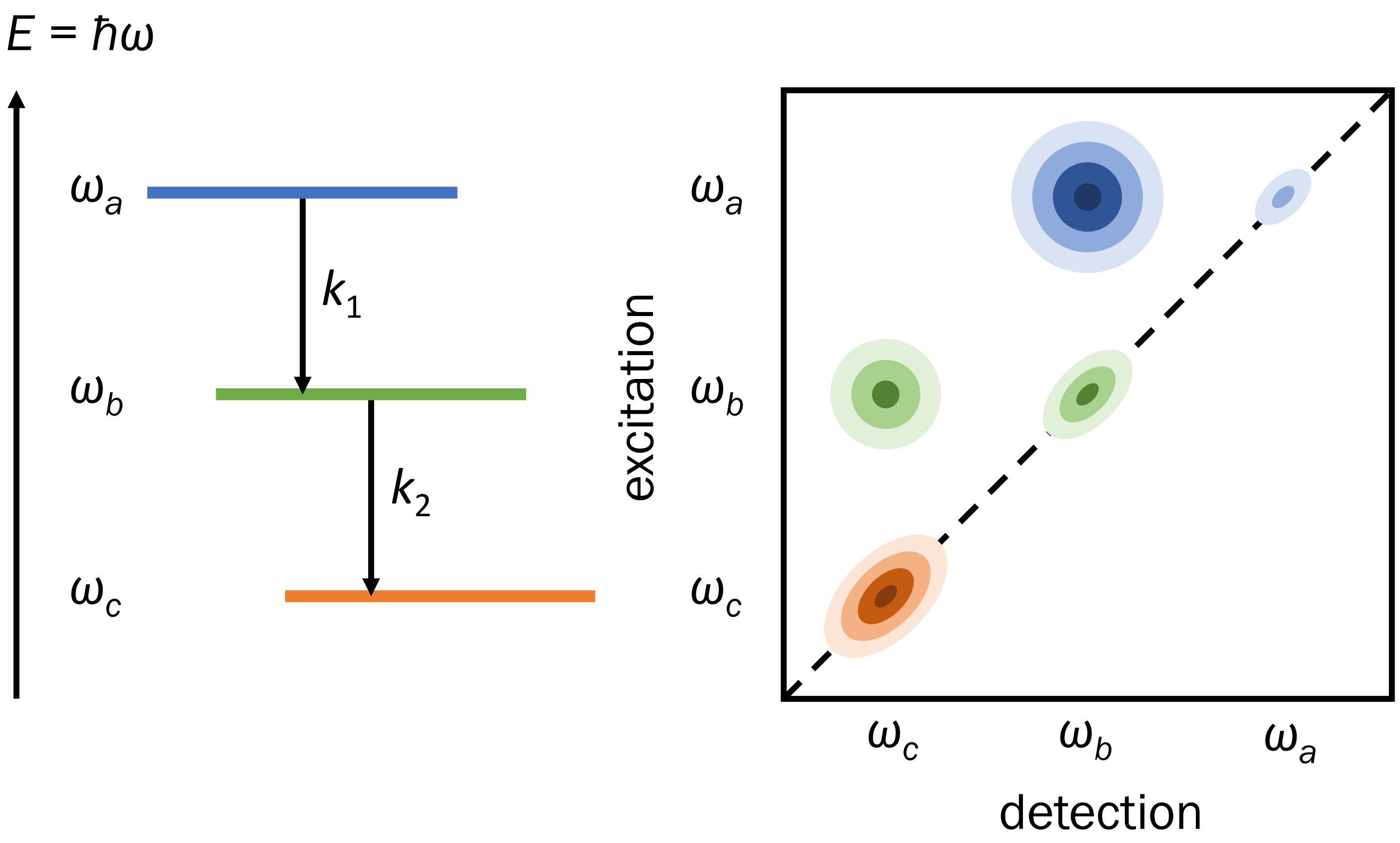
- Broadband fourier-transform 2DES

FT 2DES – PULSE SEQUENCE



$\boldsymbol{\tau}$	–	coherence time	–	oscillation frequency ω_τ
$\boldsymbol{T_w}$	–	waiting time	–	population transfer
$\boldsymbol{t}$	–	detection time	–	echo signal frequency ω_t

2D ELECTRONIC SPECTRA

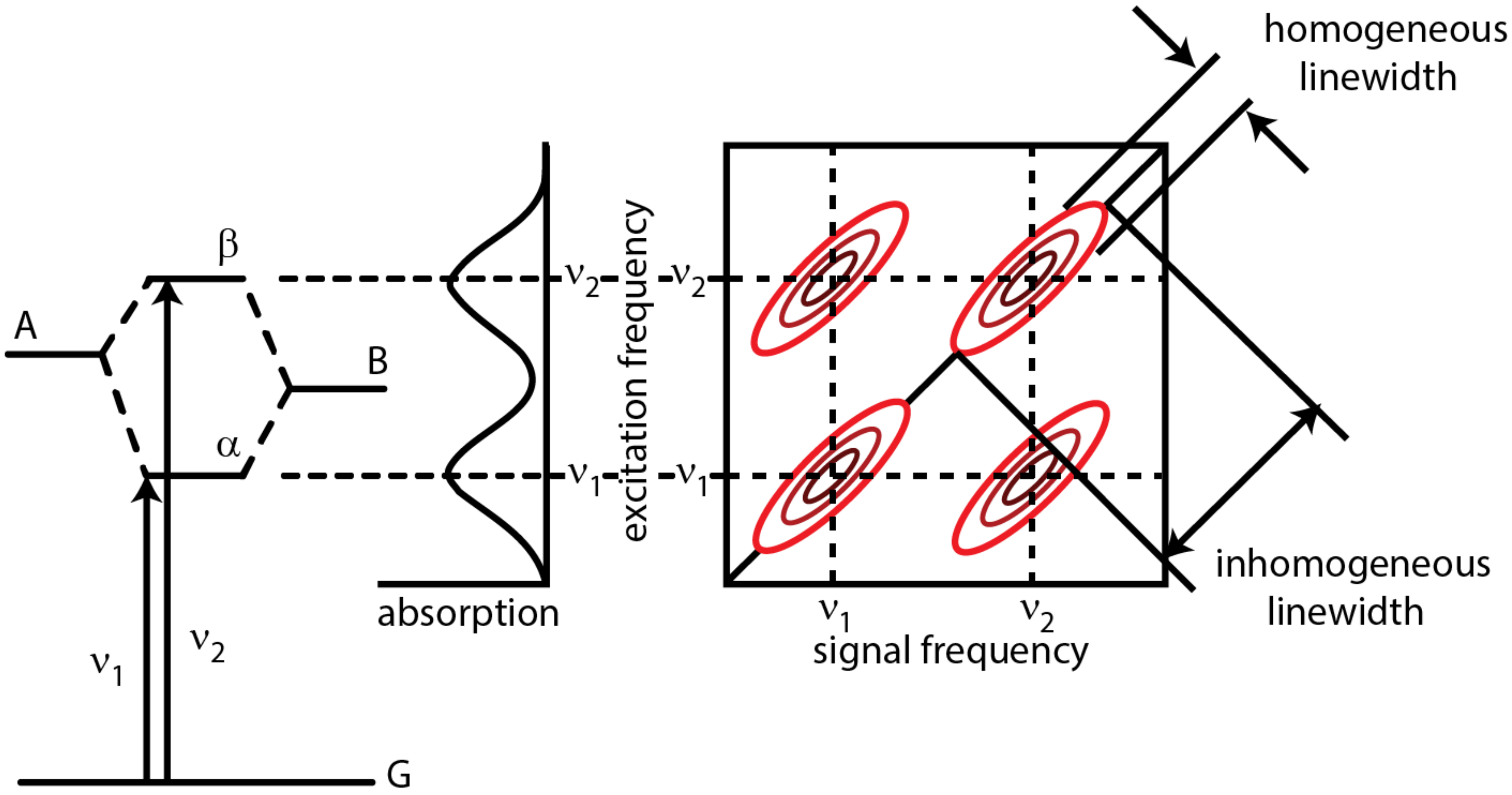


Schematic 2D electronic spectrum of a coupled three-level system

The 2D electronic spectrum

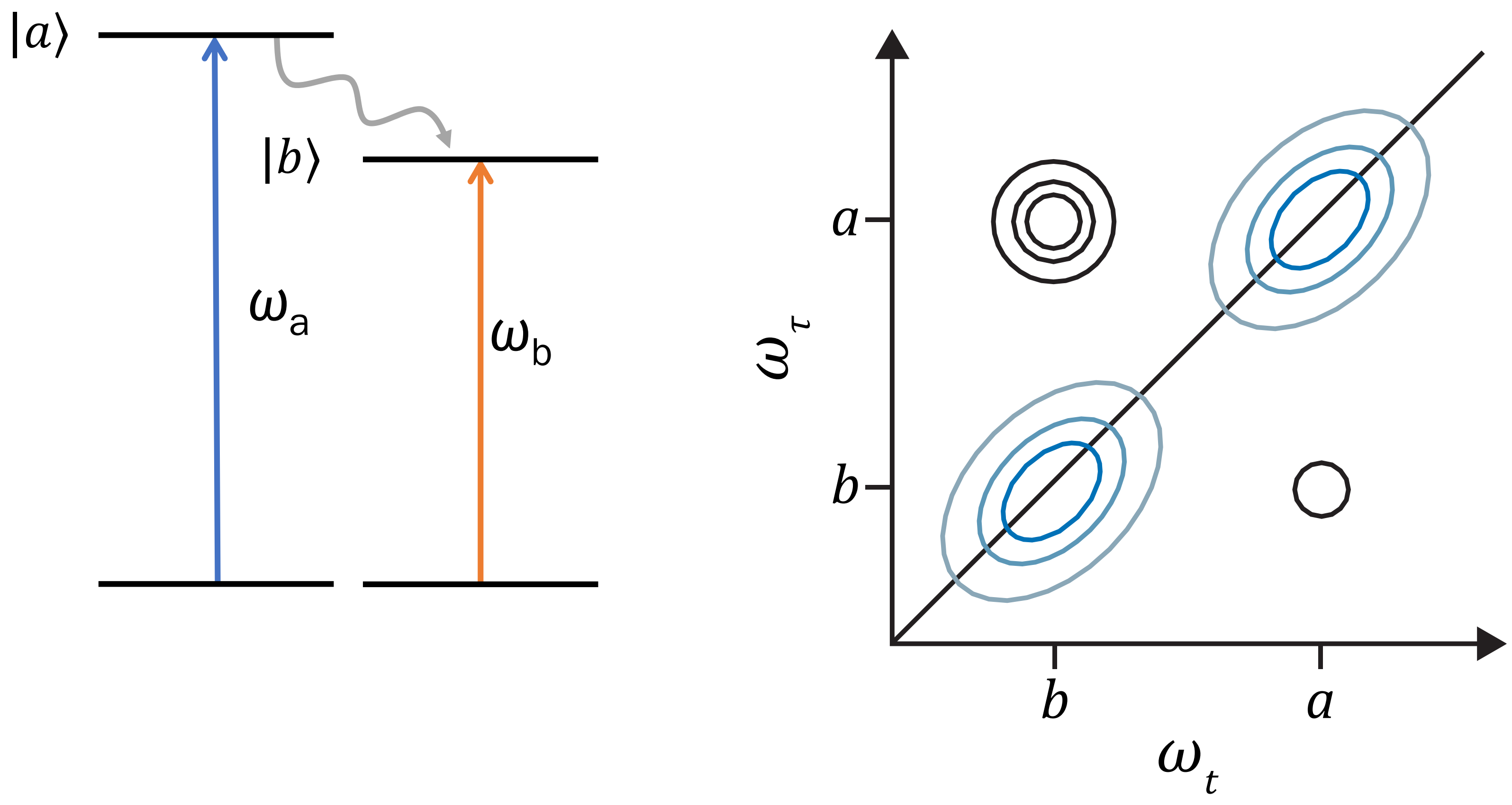
- Is a joint probability:
- The probability to find the system in state Y after excitation of state X
- Diagonal peaks – correspond to bands in the linear absorption spectrum
- Off-diagonal peaks (cross-peaks) show coupling between states

2D ELECTRONIC SPECTROSCOPY – EXCITONIC COUPLING



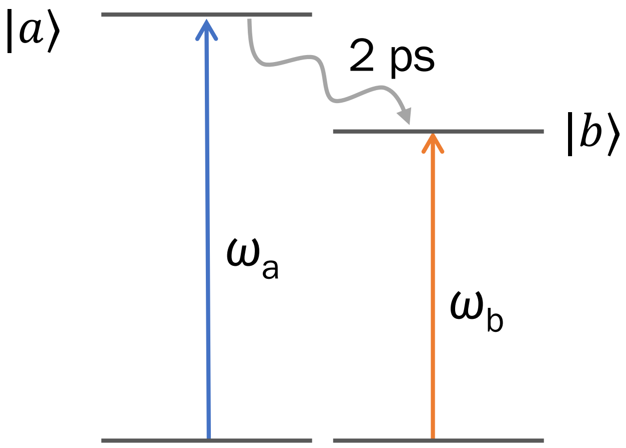
Fassioli *et al.* (2014) *JRS Interface*

2D ELECTRONIC SPECTROSCOPY – RESOLVING ENERGY TRANSFER

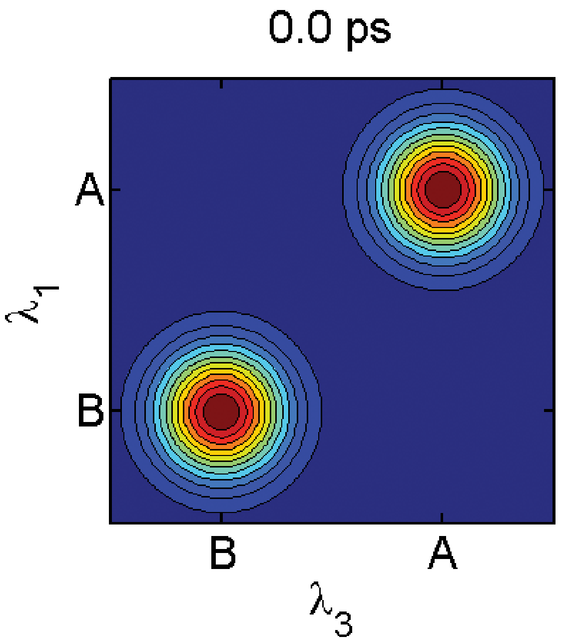


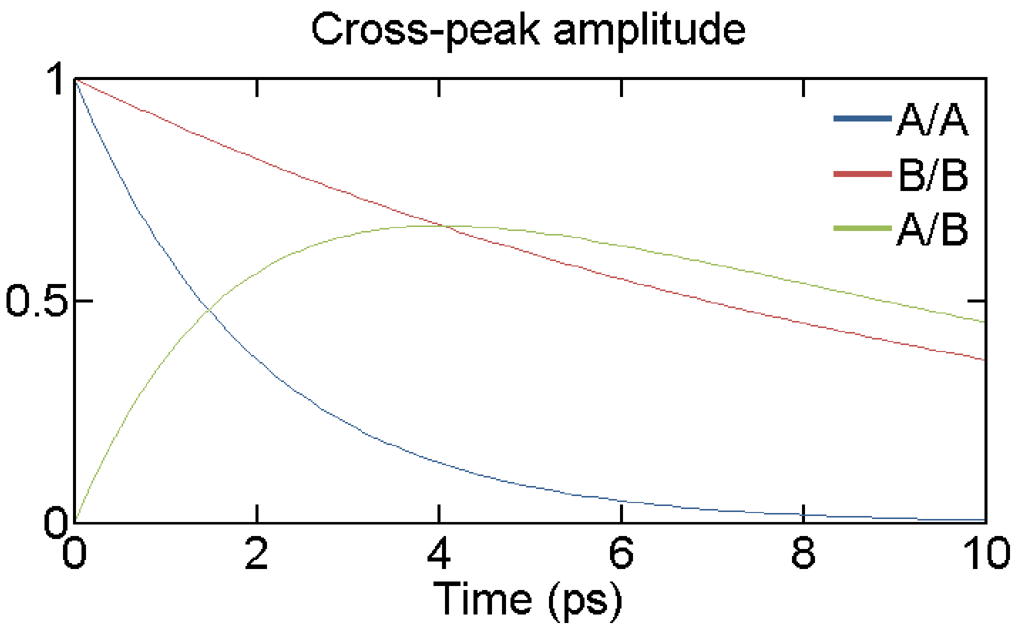
Cross peaks in the 2D spectrum reveal energy transfer

TRANSIENT 2D ELECTRONIC SPECTROSCOPY

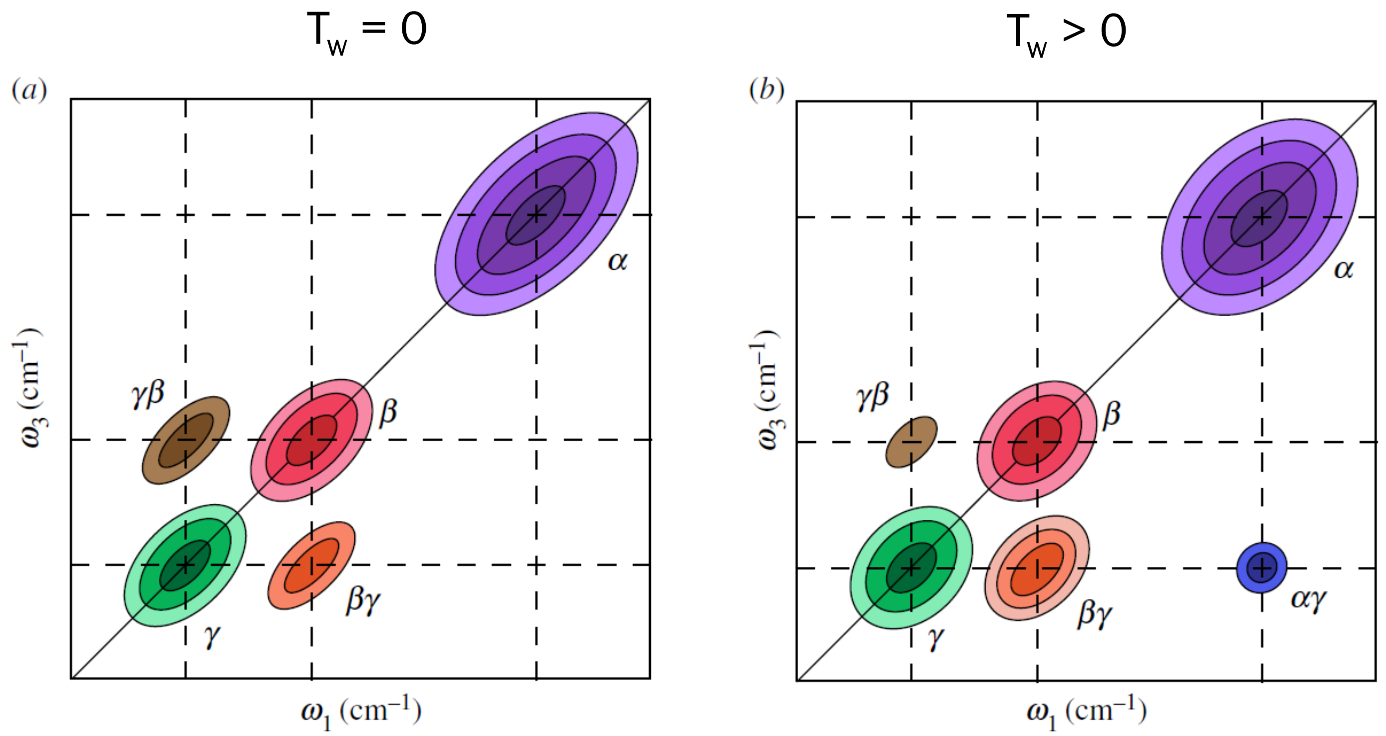


- Cross-peak at (λ_1 = A, λ_3 = B) reflects energy transfer from $|a\rangle$ to $|b\rangle$
- λ_1 = A – donor's Abs wavelength
- λ_3 = B – acceptor's Abs wavelength





EXCITONIC COUPLING AND ENERGY TRANSFER



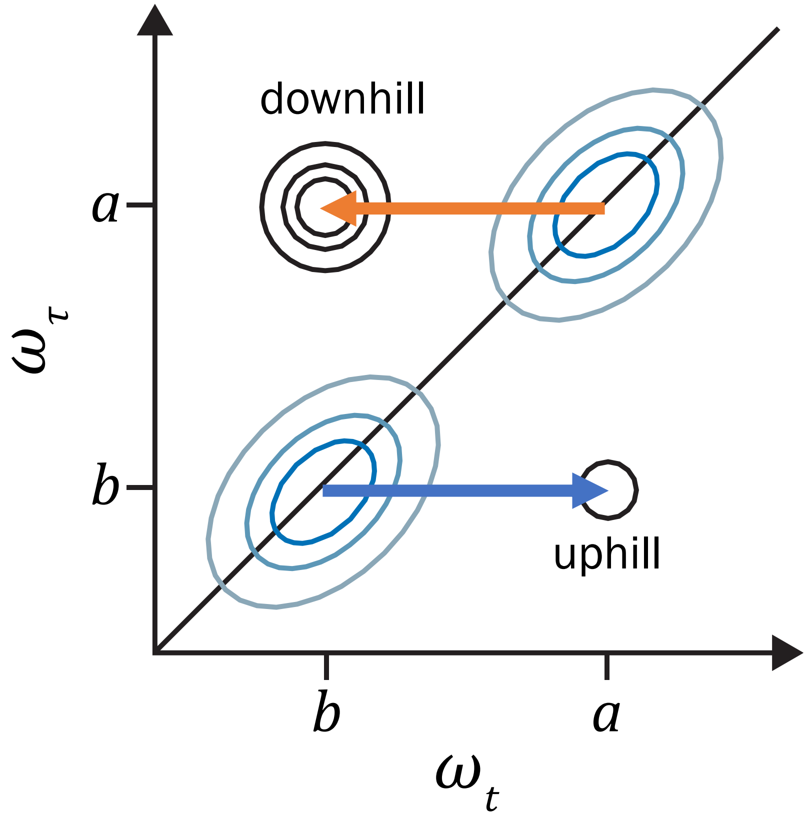
Oliver (2018) *R Soc open sci*

DOWNHILL VS UPHILL ENERGY TRANSFER

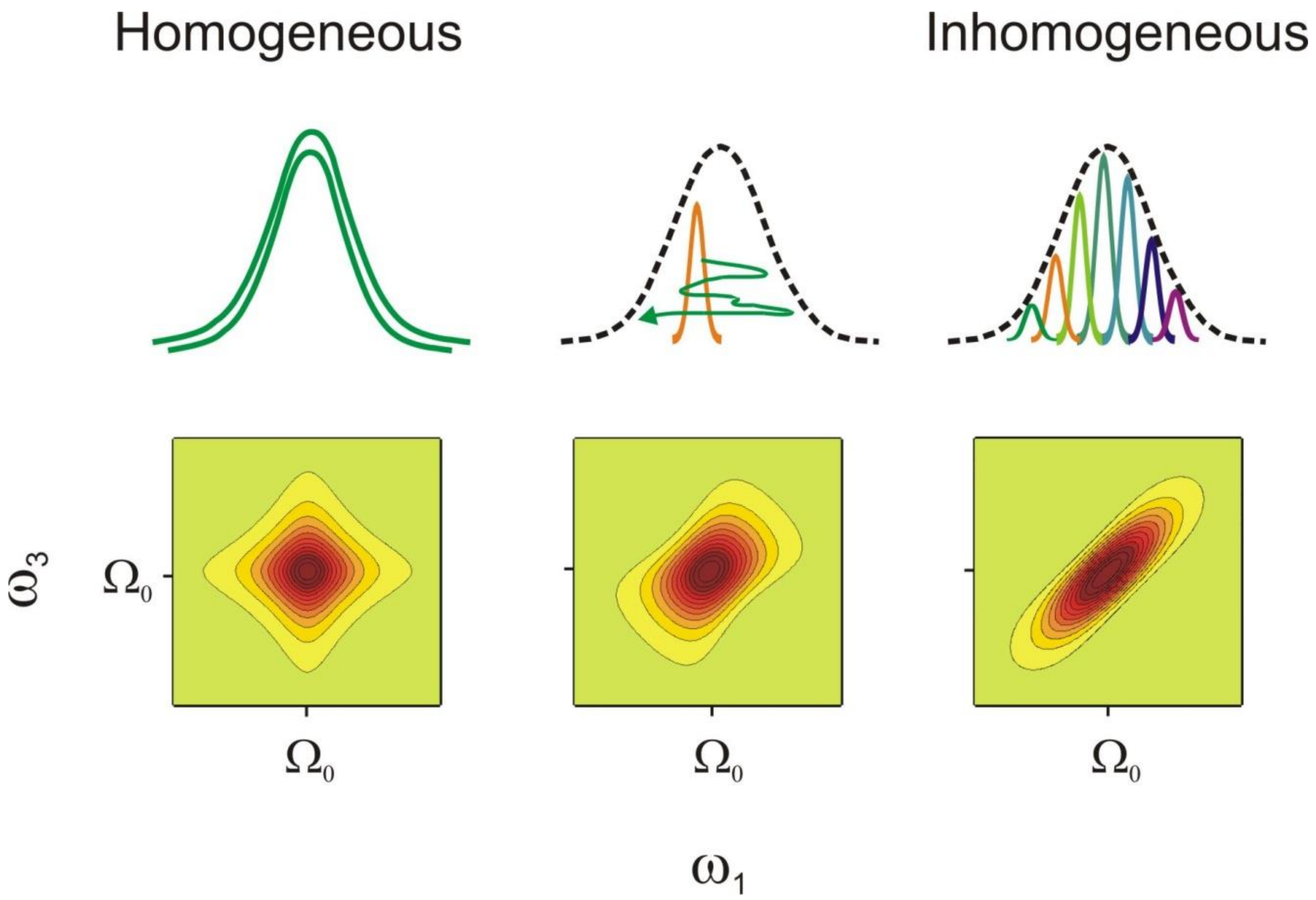
$$\mathrm{A} \underset{k_{\mathrm{ba}}}{\overset{k_{\mathrm{ab}}}{\rightleftarrows}} \mathrm{B}$$

$$\frac{k_{\mathrm{ab}}}{k_{\mathrm{ba}}} = \mathrm{e}^{-\frac{\Delta E}{k_B T}}$$

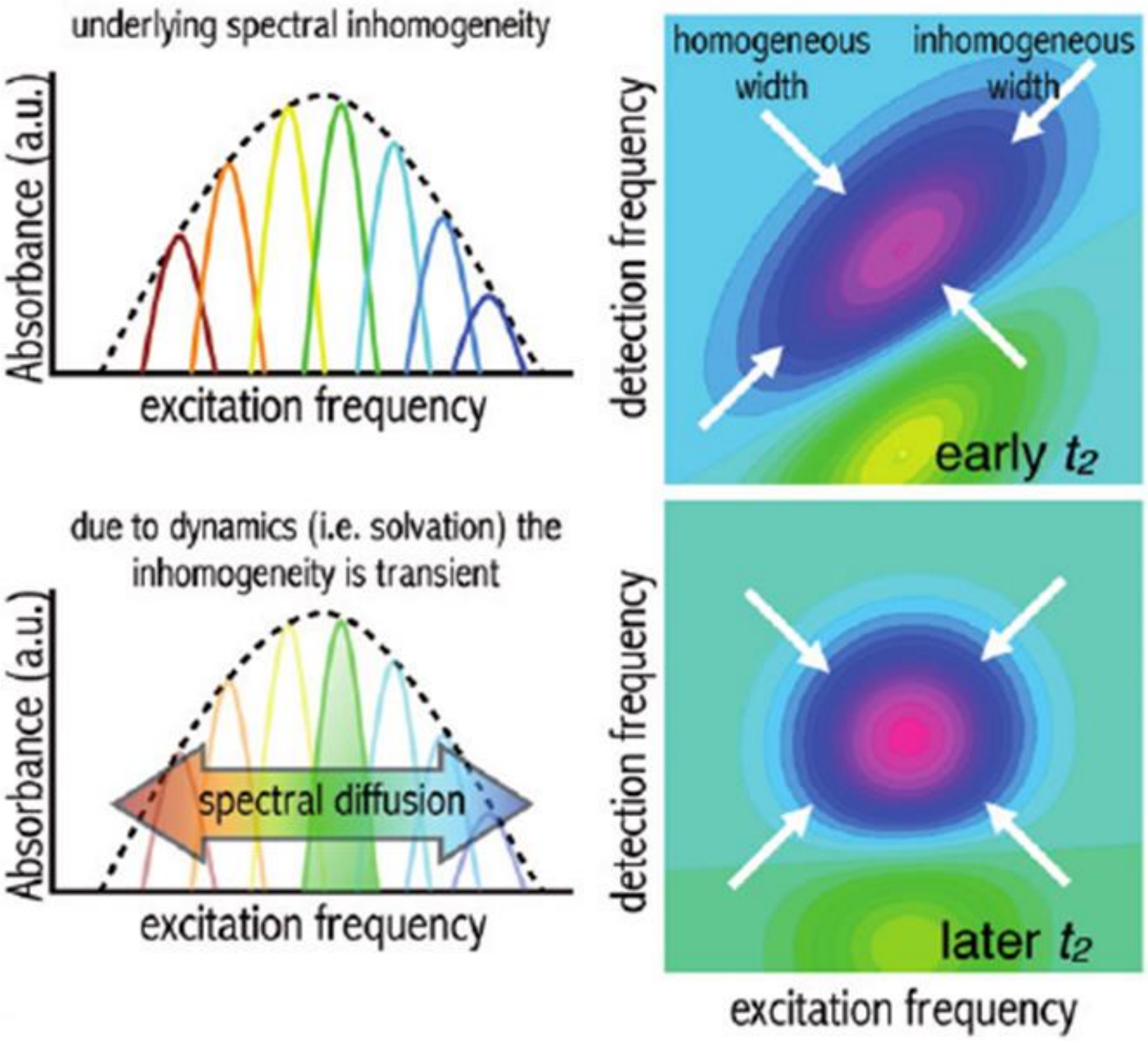
Detailed balance
(Boltzmann distribution)



2D LINESHAPES

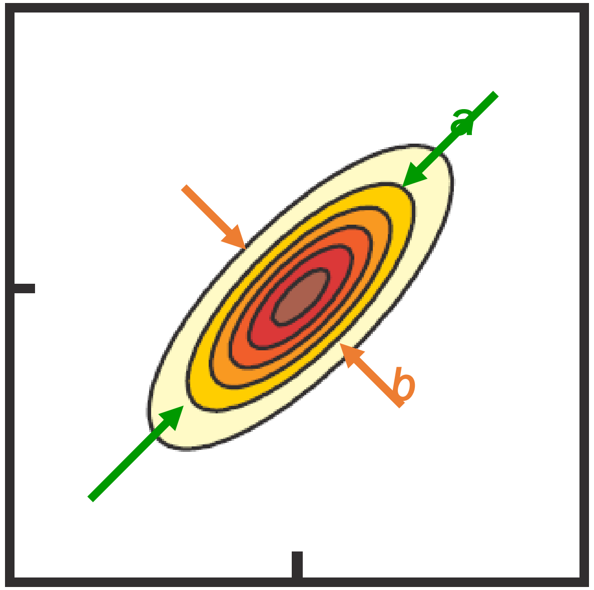


SPECTRAL BROADENING AND SPECTRAL DIFFUSION

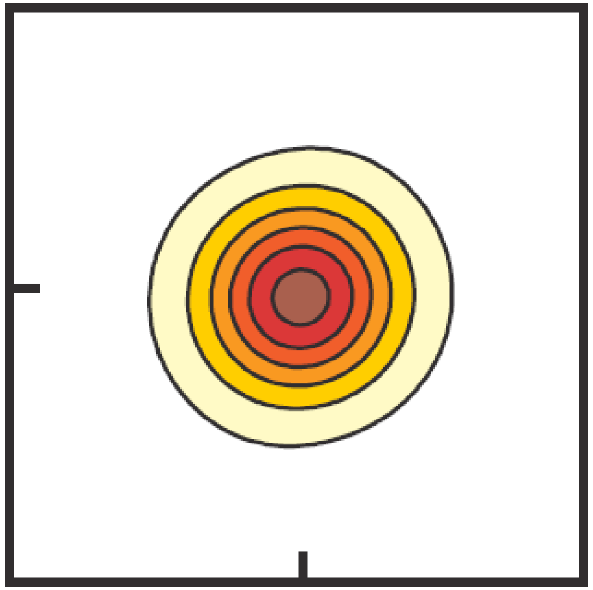


2D LINESHAPES: LOSS OF FREQUENCY CORRELATION

$\tau_2 \ll \tau_c$



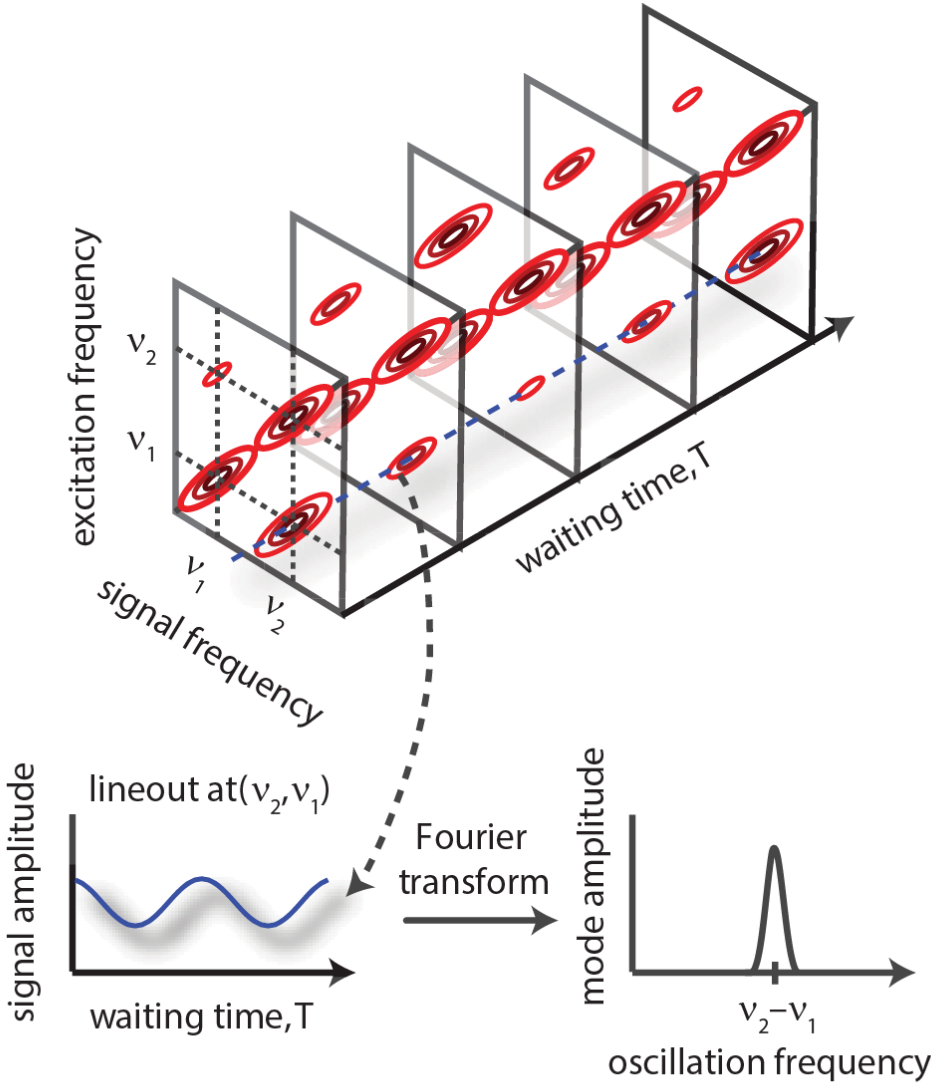
$\tau_2 \gg \tau_c$



Ellipticity

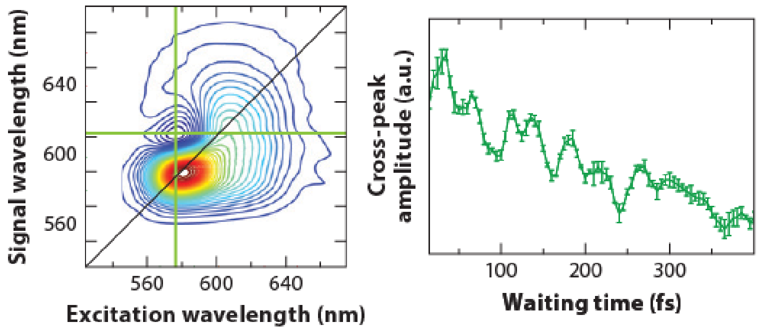
$$E = \frac{a^2 - b^2}{a^2 + b^2}$$

COHERENT DYNAMICS



- Exciton coherence:
  - Coherent superposition of eigenstates
  - Cross-peaks oscillate with T_w
  - The oscillation frequency reflects the energy split

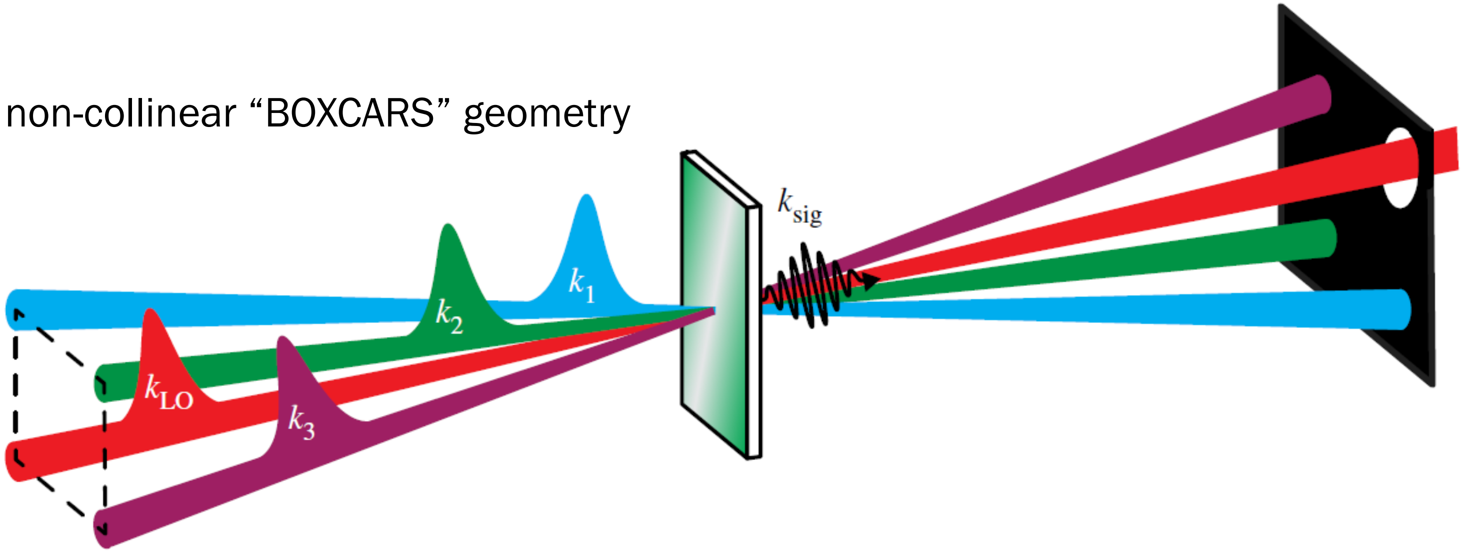
Coherence dynamics in PC645

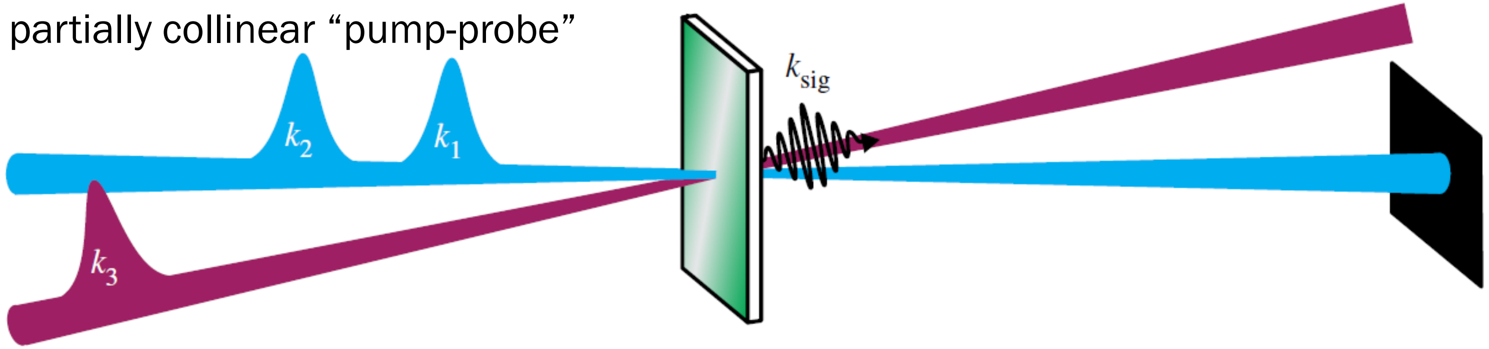


Chenu & Scholes 2015 *Annu Rev Phys Chem*

TECHNICAL IMPLEMENTATIONS

TECHNICAL IMPLEMENTATIONS OF 2DES





Oliver (2018) *R Soc open sci*

BOXCARS geometry

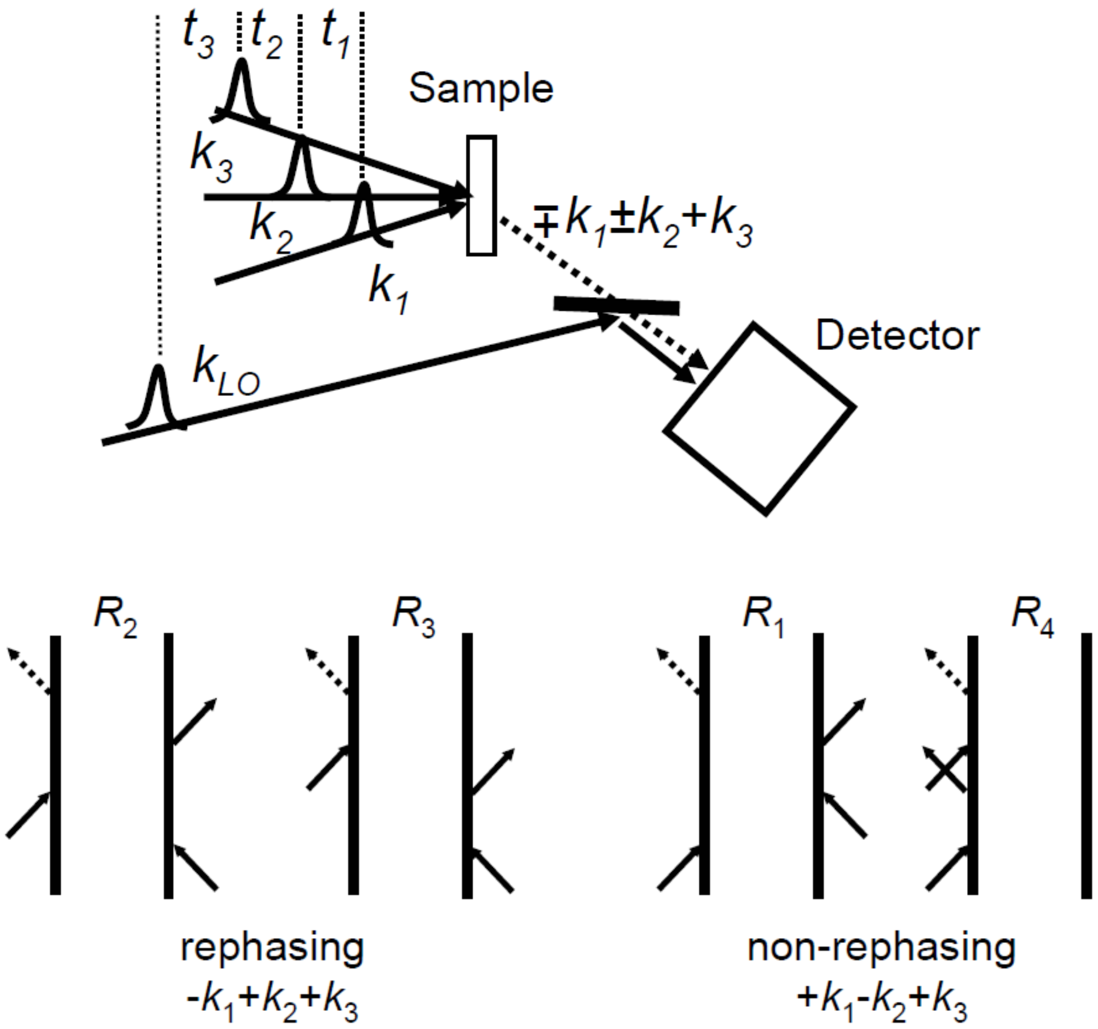
- ✓ Background-free
- ✓ Signals of interest detected in the phase-matching direction
- ✓ Separation of rephasing/non-rephasing signal
- ✓ Full polarization control possible
- ✗ The absorptive signal is a sum of two experiments (phasing issues)

Pump-probe geometry

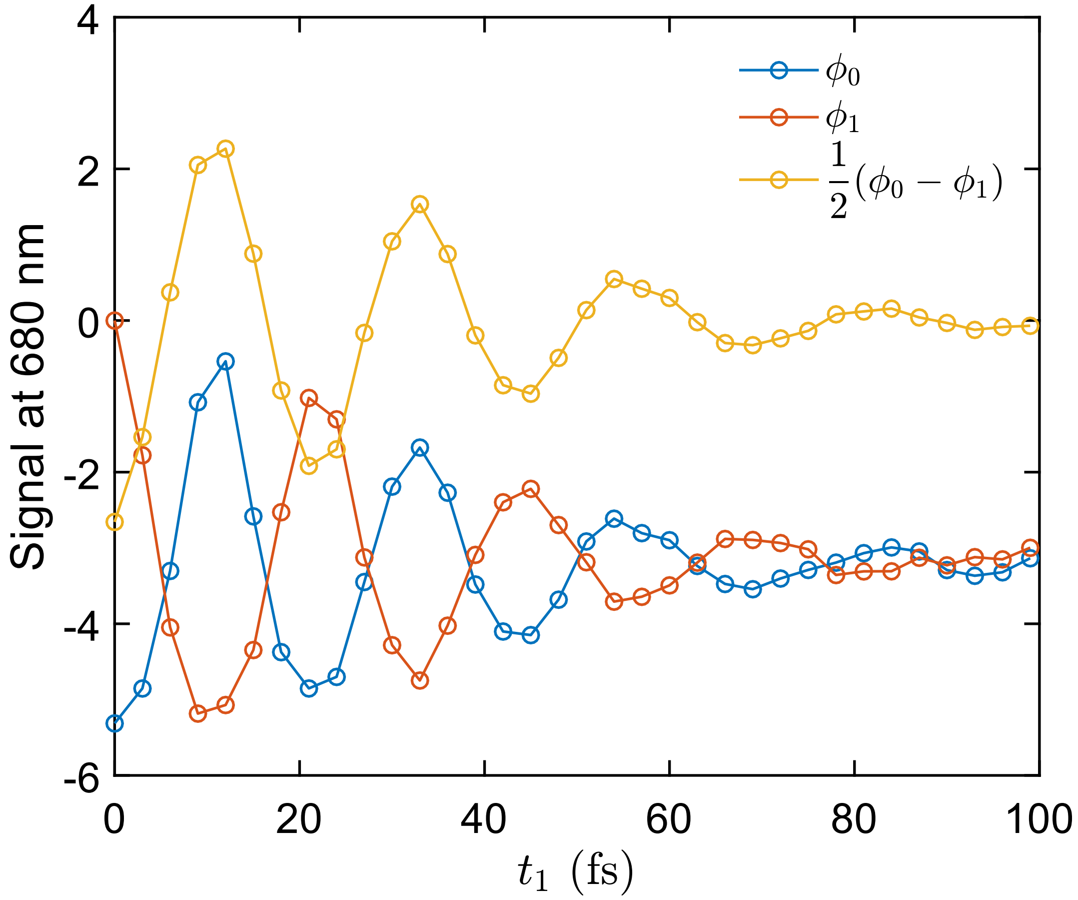
- ✗ The signal and background (probe) are collinear
- ✗ No full polarization control
- ✓ Signal isolated by phase cycling
- ✓ Simpler setup
- ✓ Less data points (partial RF)
- ✓ Absorptive shape, no phase error

PHASE MATCHING VS PHASE CYCLING

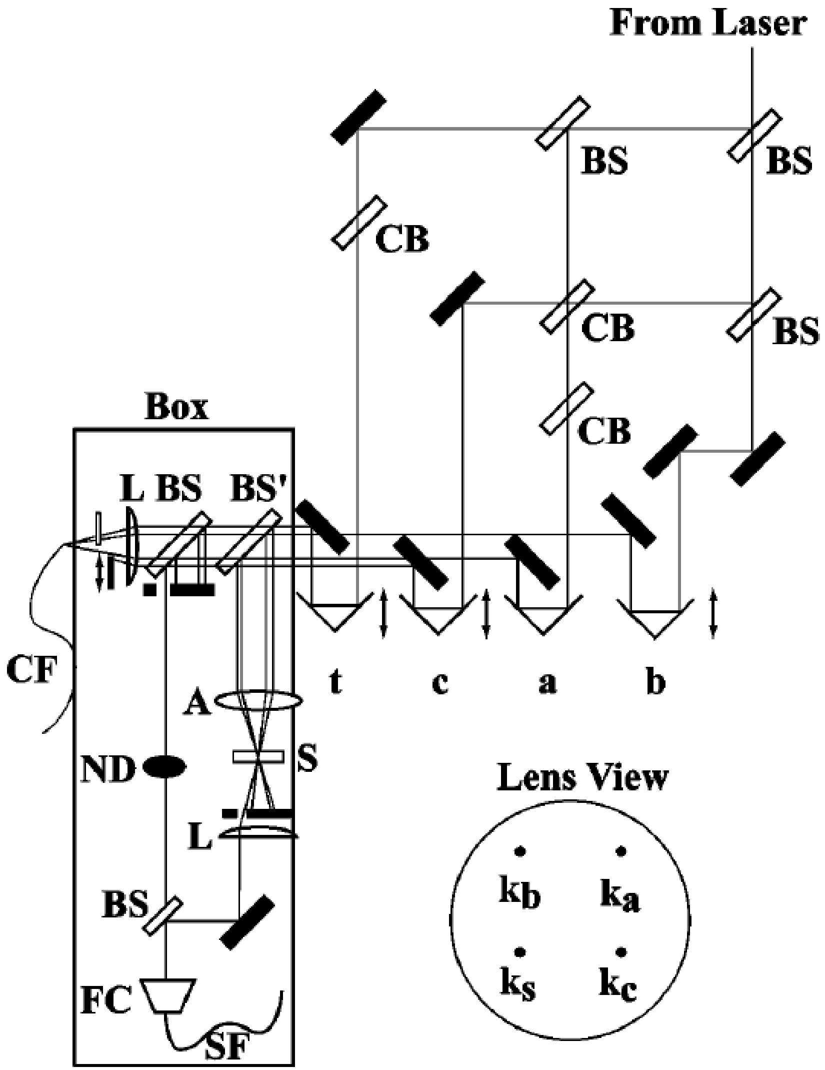
Phase matching (BOXCARS)



Phase cycling (Pump-probe geometry)

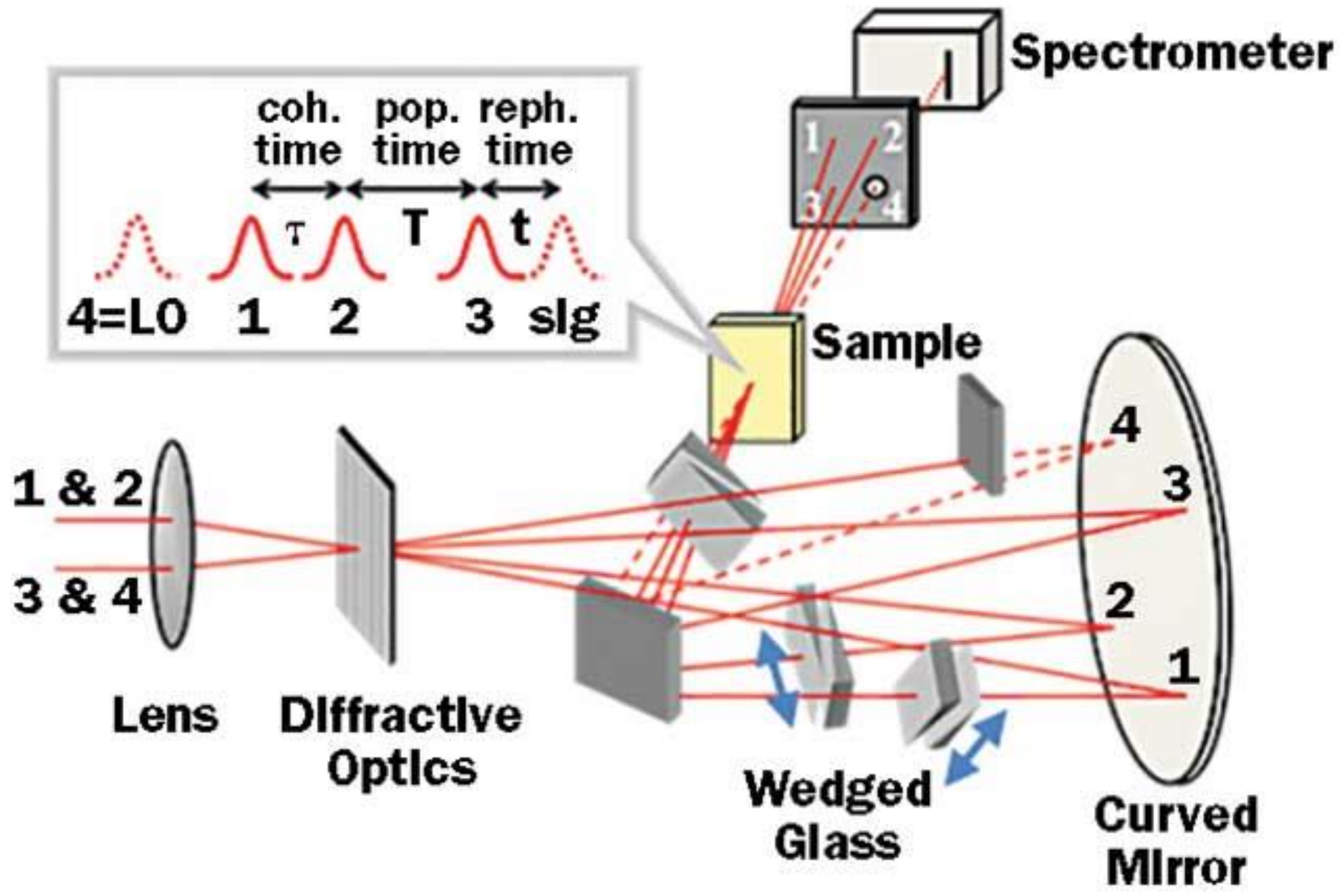


INTERFEROMETER-BASED BOXCARS SETUP



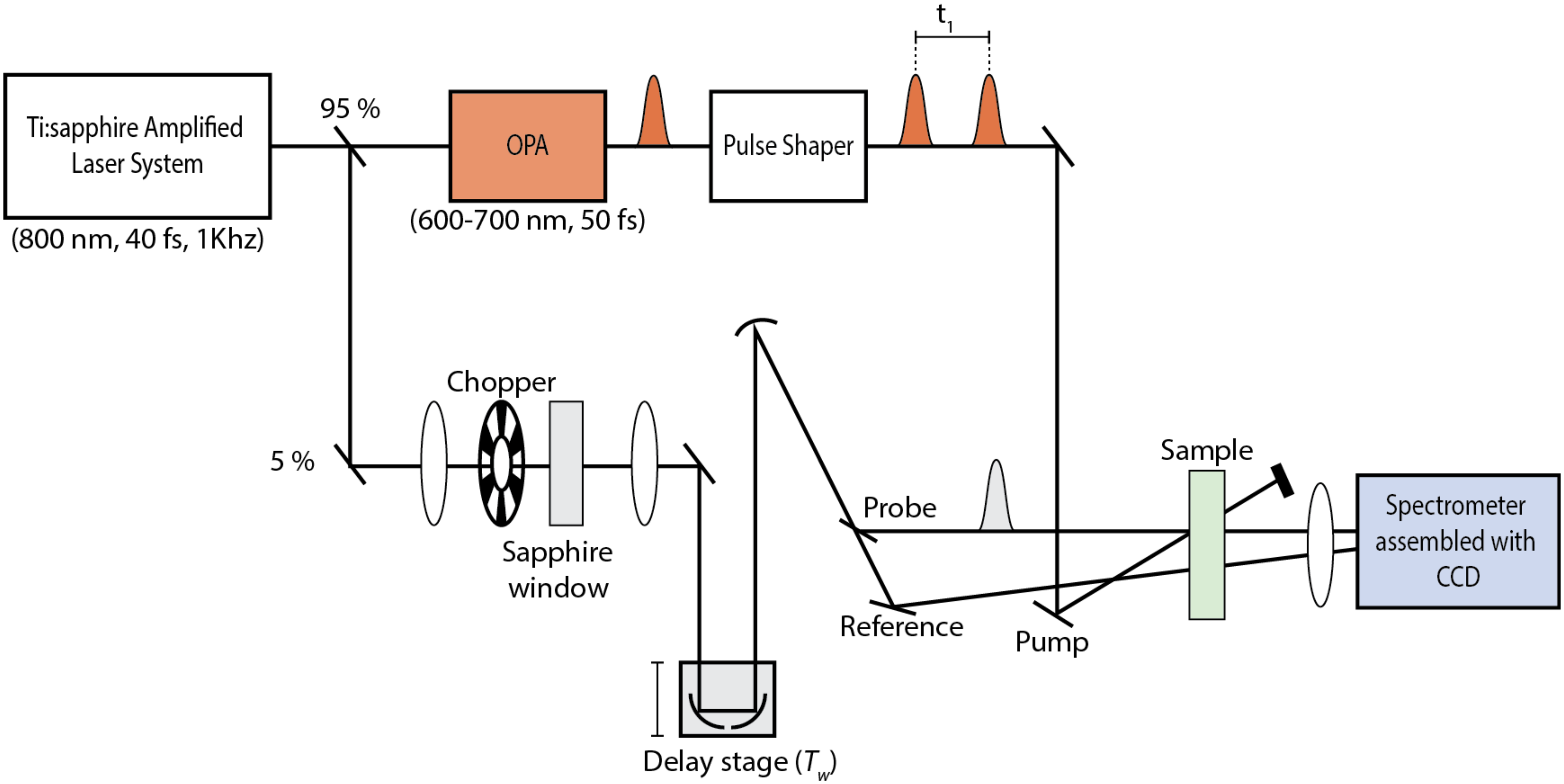
Jonas (2003) Annu. Rev. Phys. Chem.

BOXCARS SETUP USING DIFFRACTIVE OPTICS



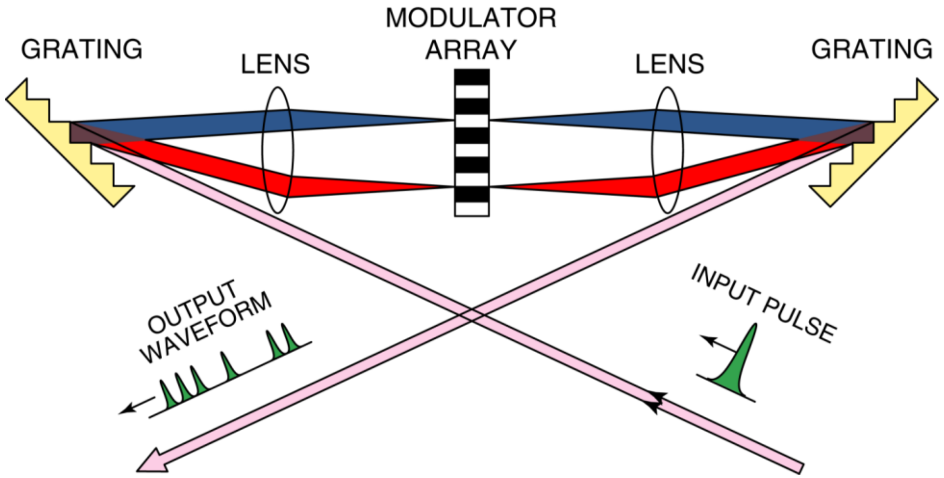
G. Fleming, UC Berkeley, USA

PULSE-SHAPER-ASSISTED PUMP-PROBE GEOMETRY SETUP

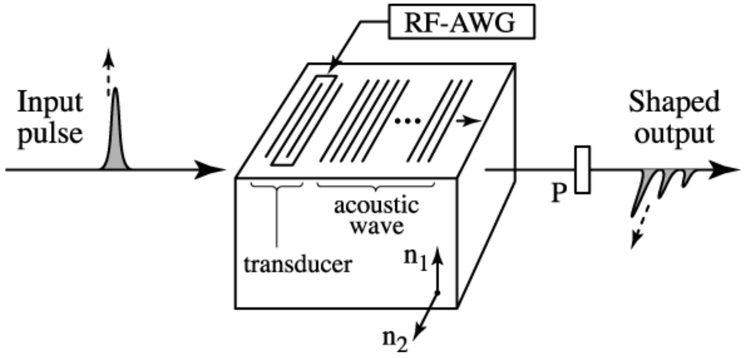


H.-S. Tan, NTU, Singapore

FT PULSE SHAPING

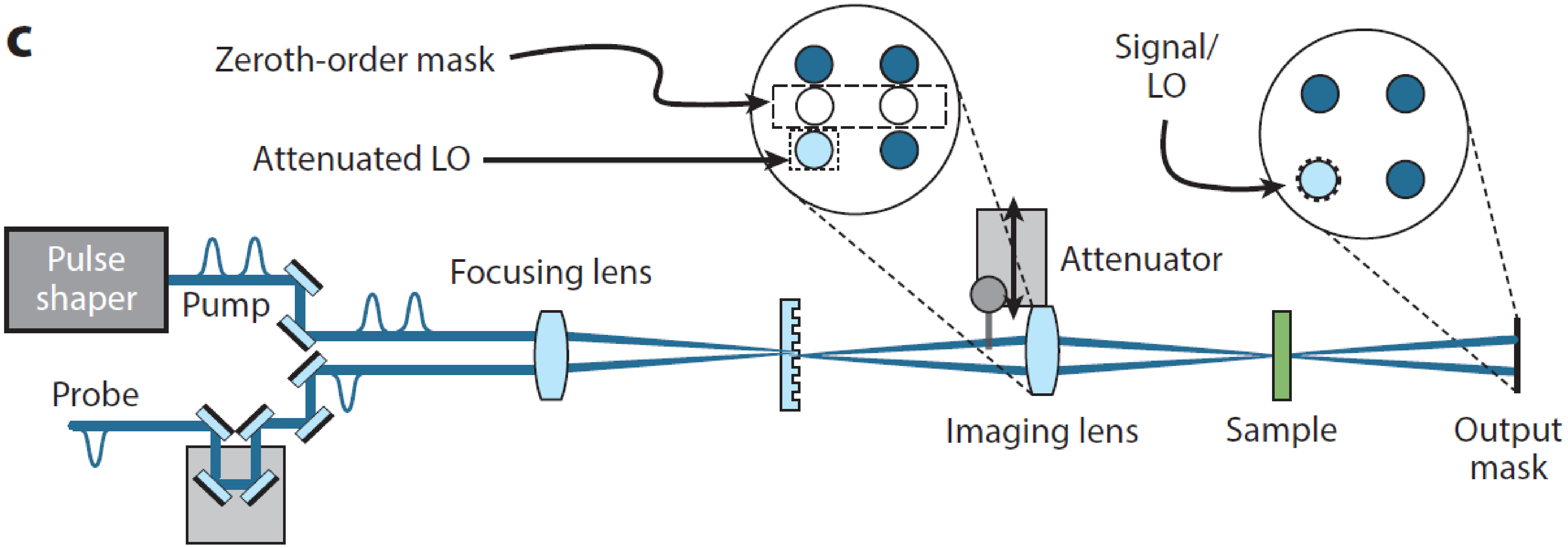


Fourier synthesis via parallel spatial/spectral modulation
Variety of spatial light modulators (**SLM**): LCD, LCM, deformable mirrors, AOM



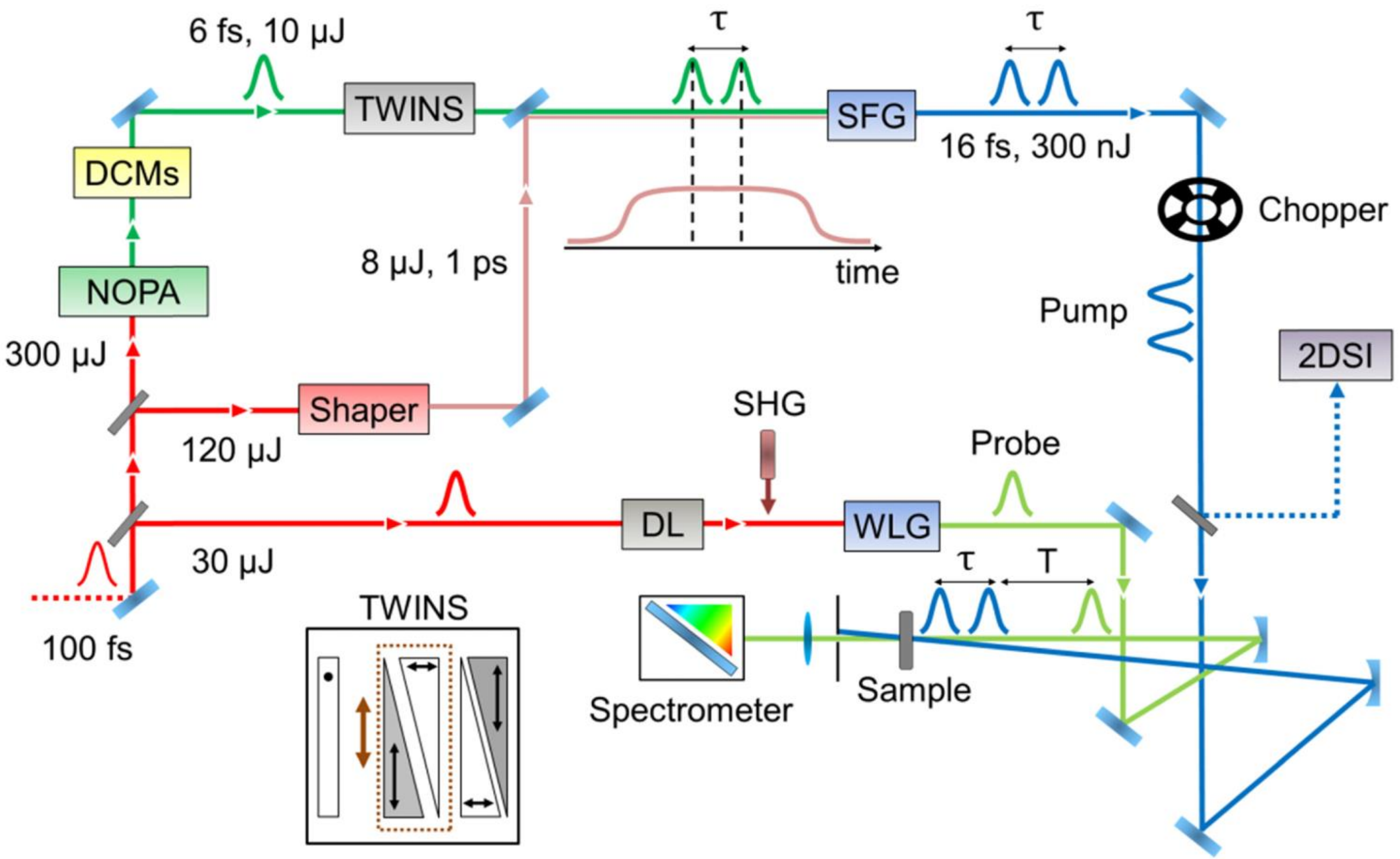
Acousto-optic Programmable Dispersive Filter (AOPDF)

HYBRID PULSE-SHAPER-DO SETUP



Fuller & Ogilvie (2015) Annu. Rev. Phys. Chem.

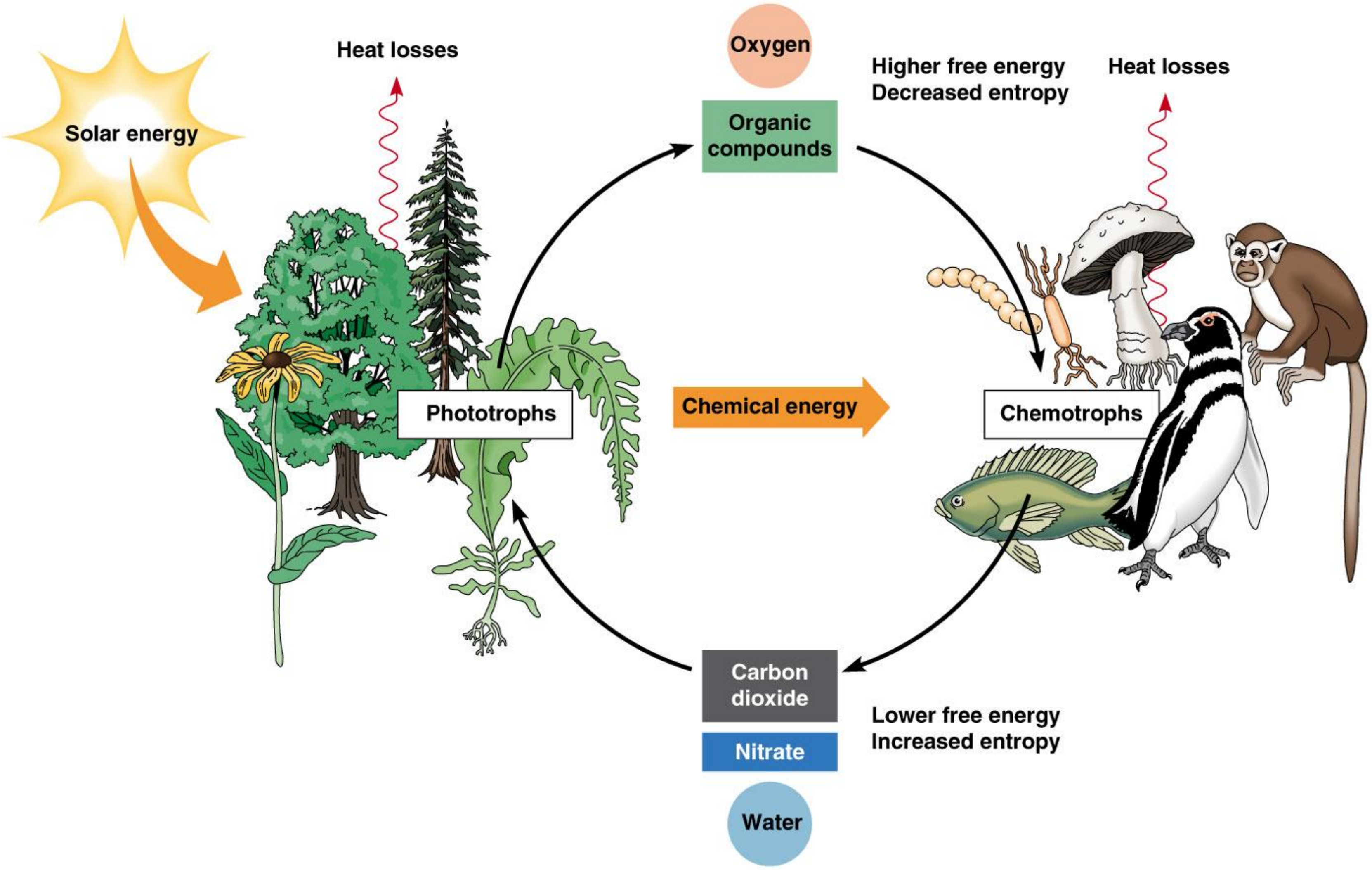
TRANSLATING WEDGE INTERFEROMETER (TWINS) SETUP



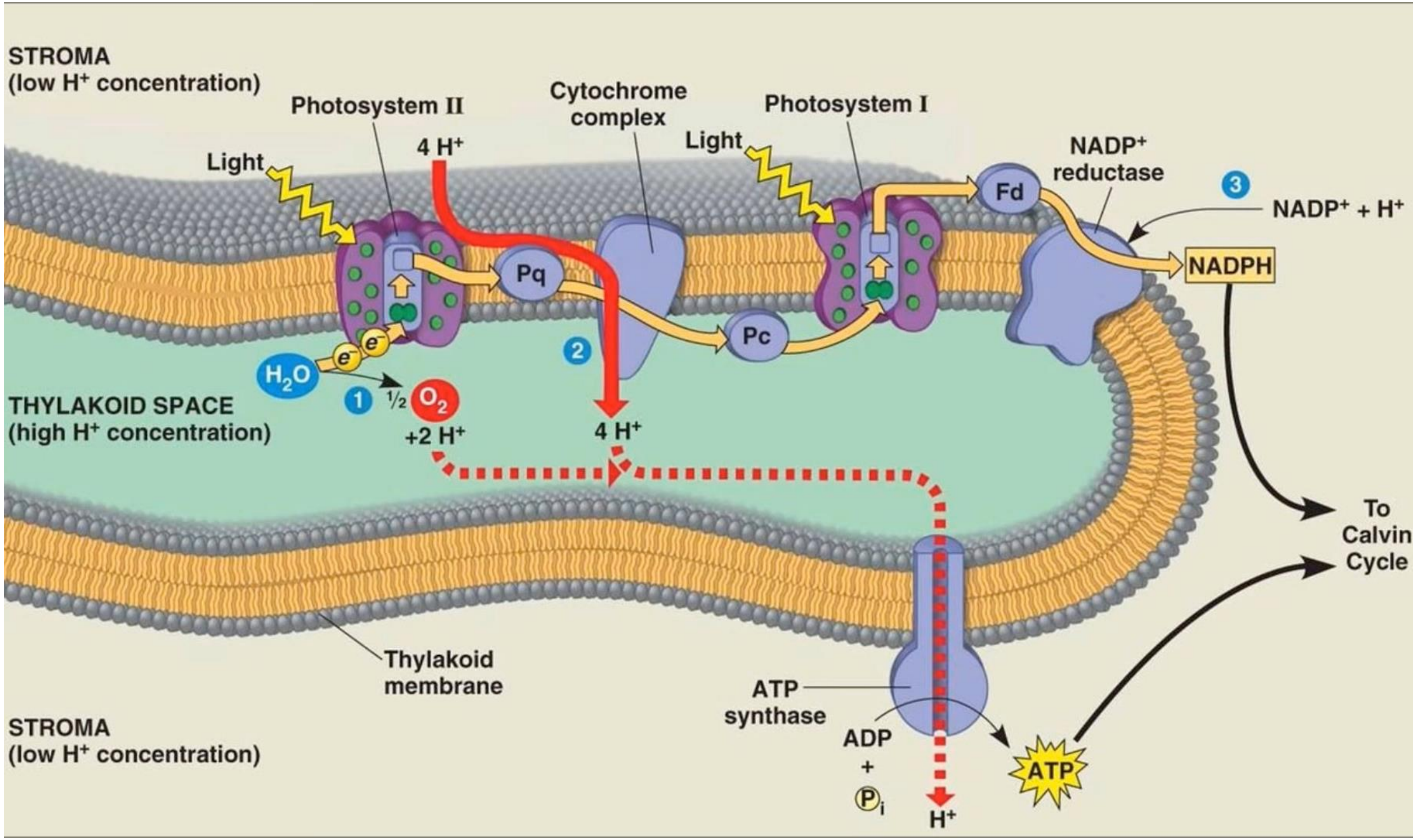
Borrego-Varrilas et al. (2016) Opt. Express

APPLICATIONS IN PHOTOSYNTHESIS

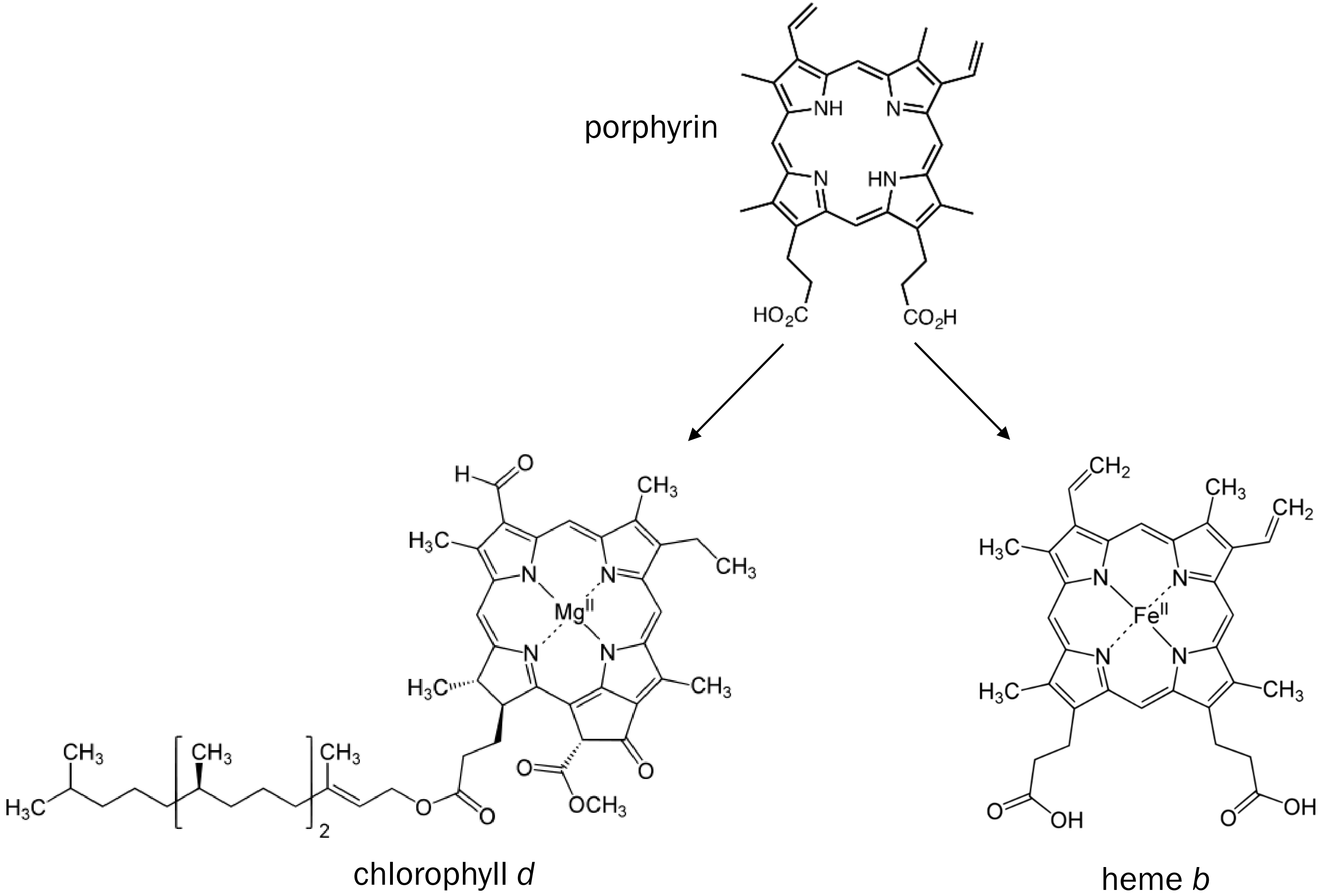
PHOTOSYNTHESIS POWERS LIFE



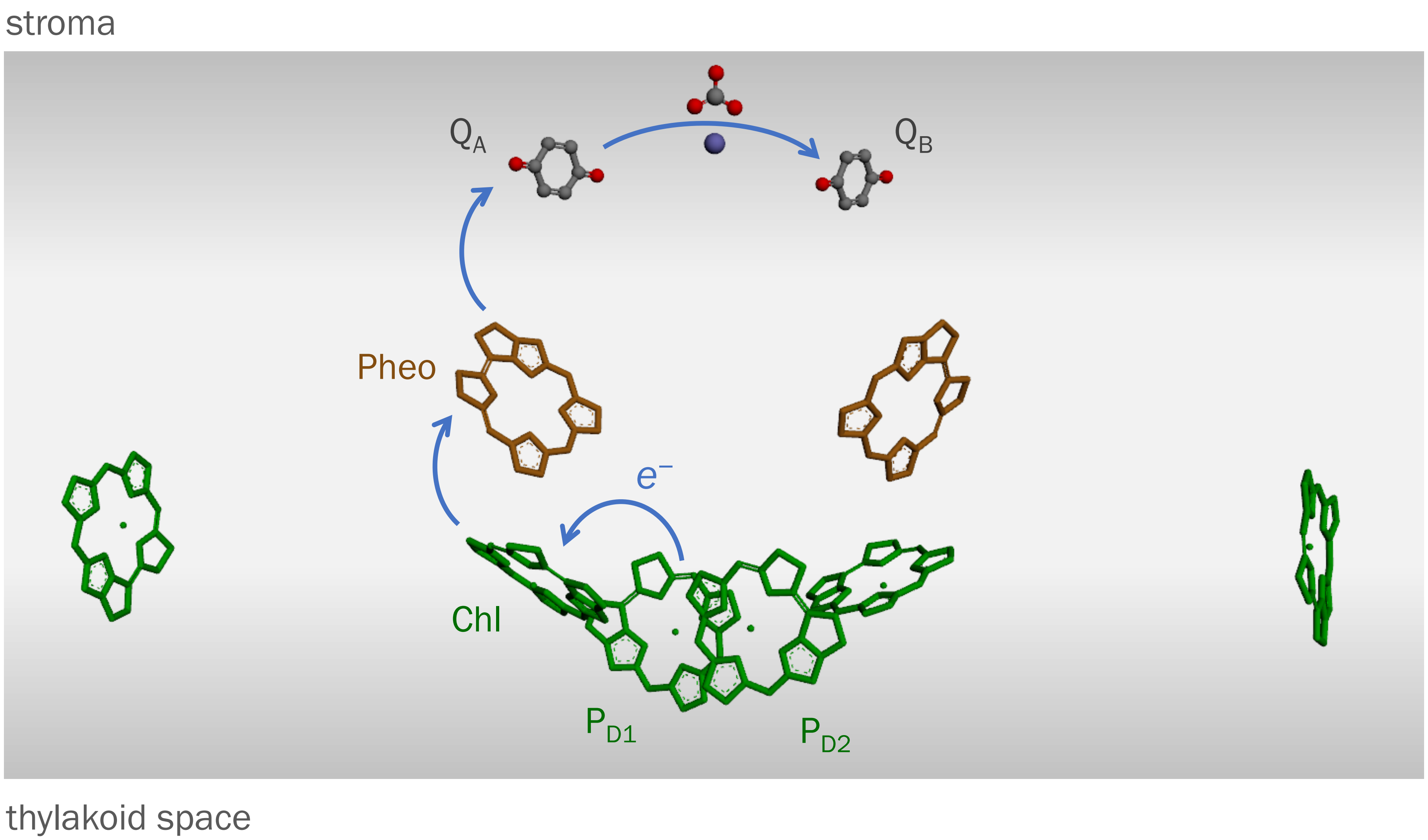
PHOTOSYNTHETIC ELECTRON TRANSPORT



CHLOROPHYLL STRUCTURE

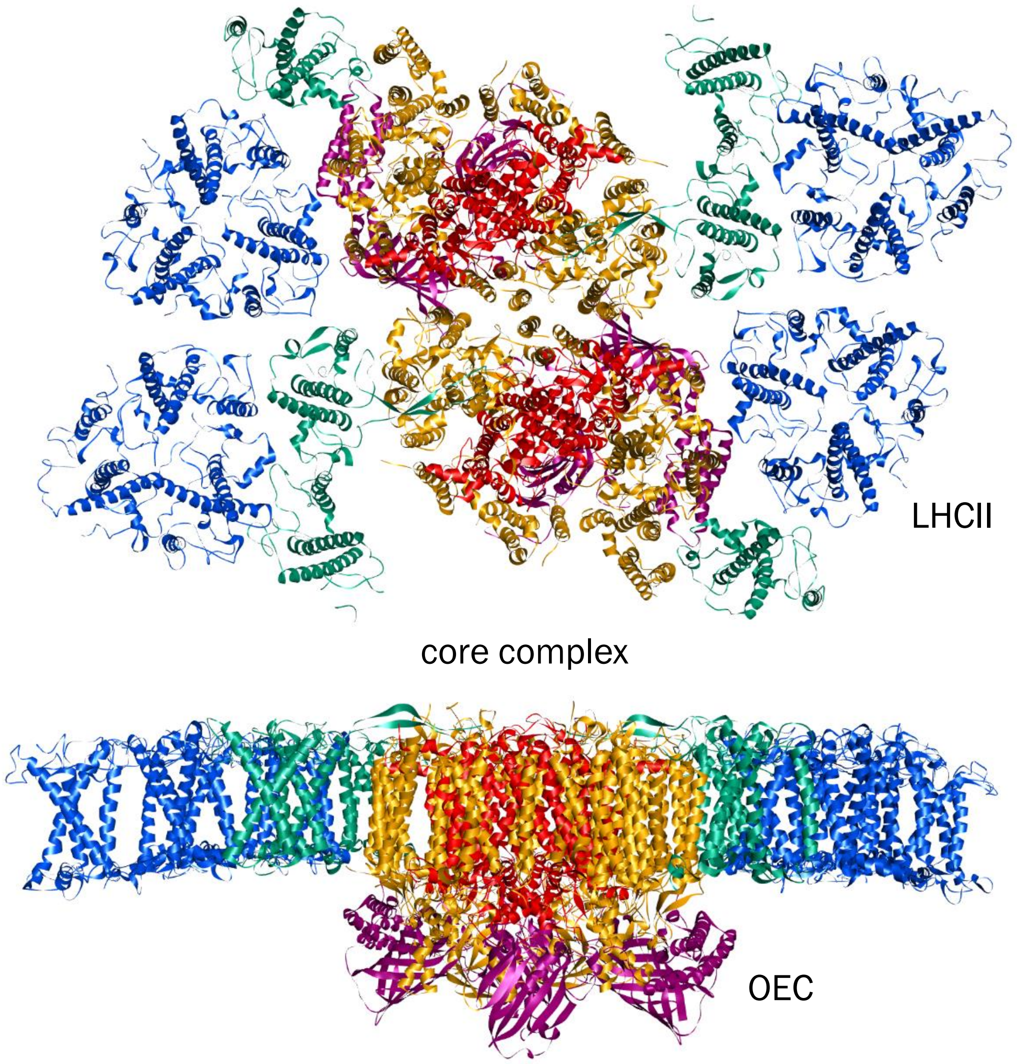


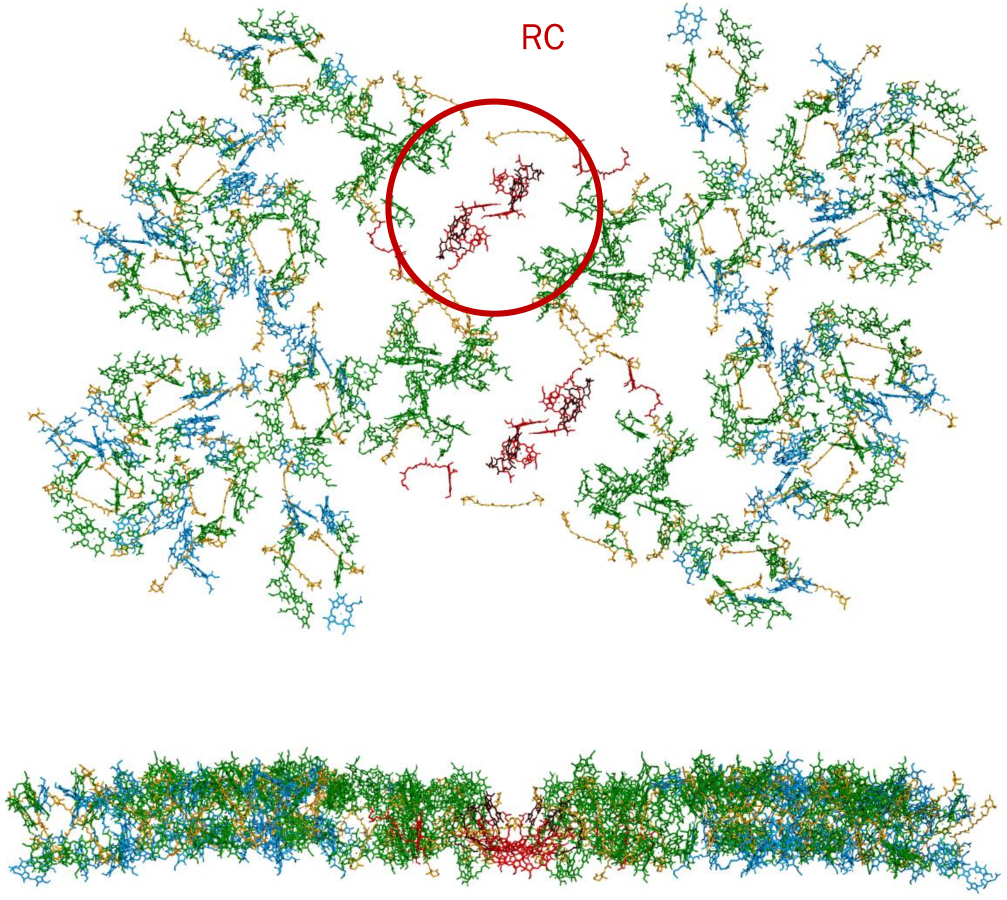
PHOTOCHEMISTRY OCCURS IN THE REACTION CENTRE



Photosystem II reaction centre

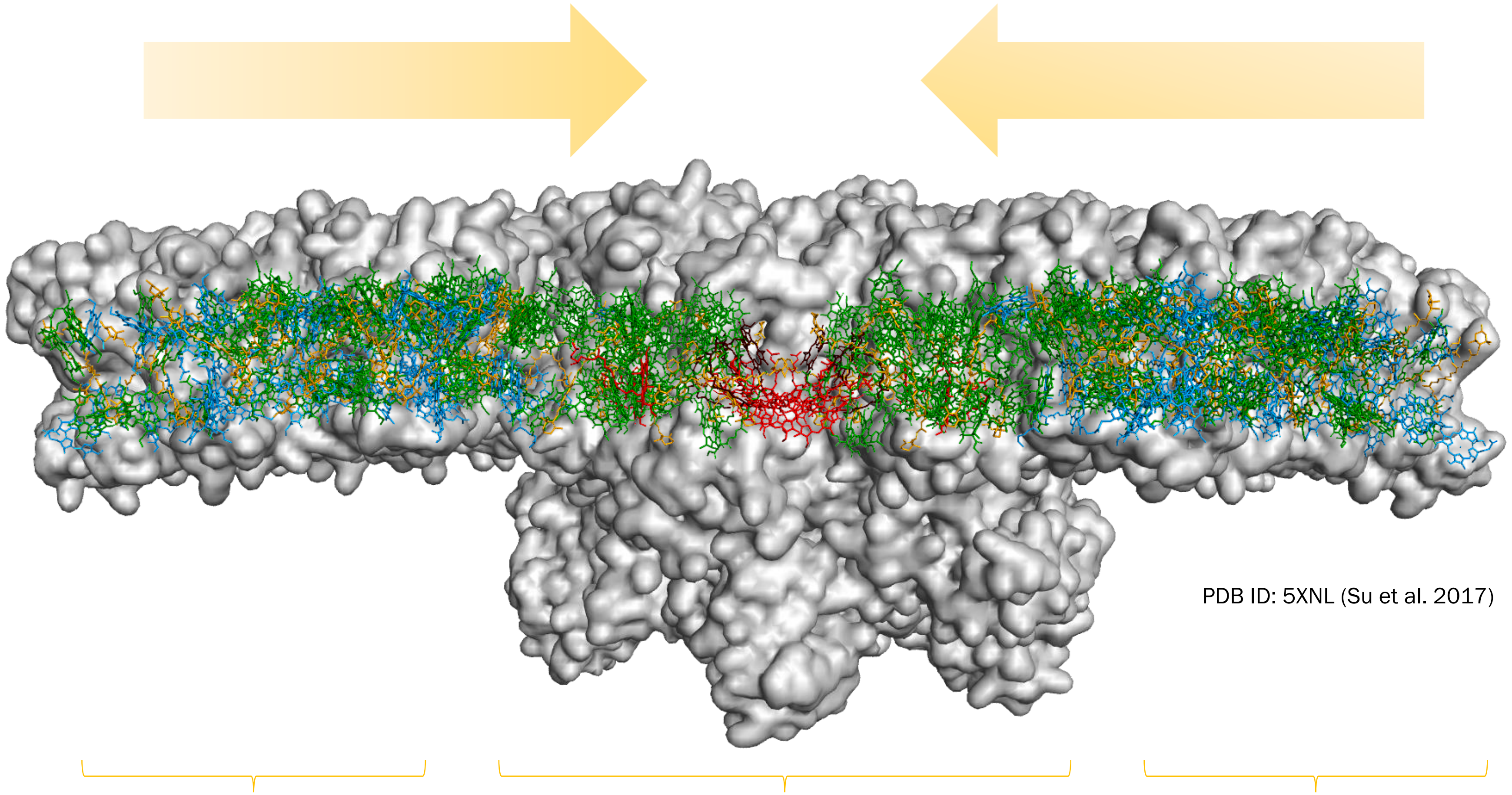
THE PSII-LHCII SUPERCOMPLEX





Su et al. 2017 Science

MOST OF THE CHLOROPHYLLS FUNCTION AS LIGHT-HARVESTING ANTENNA

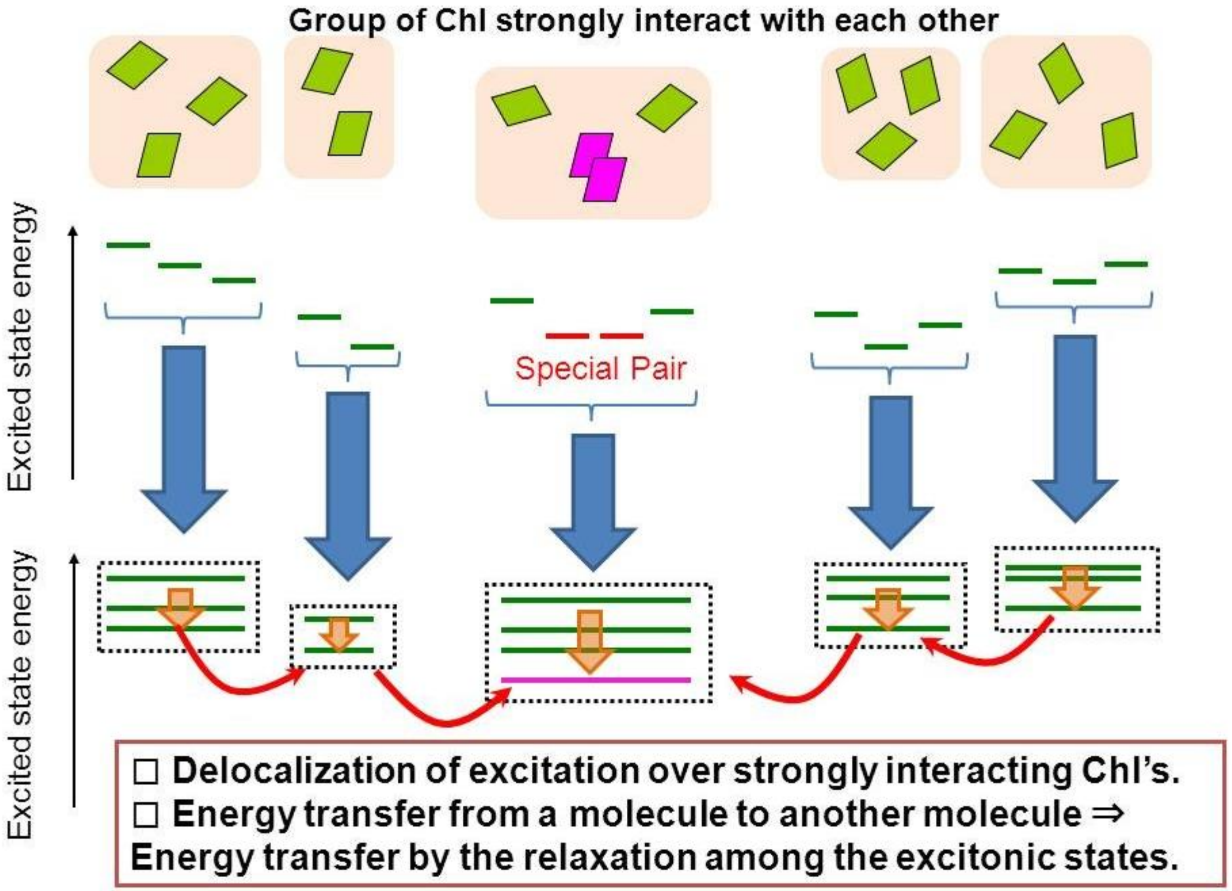


light-harvesting complexes (LHCII)

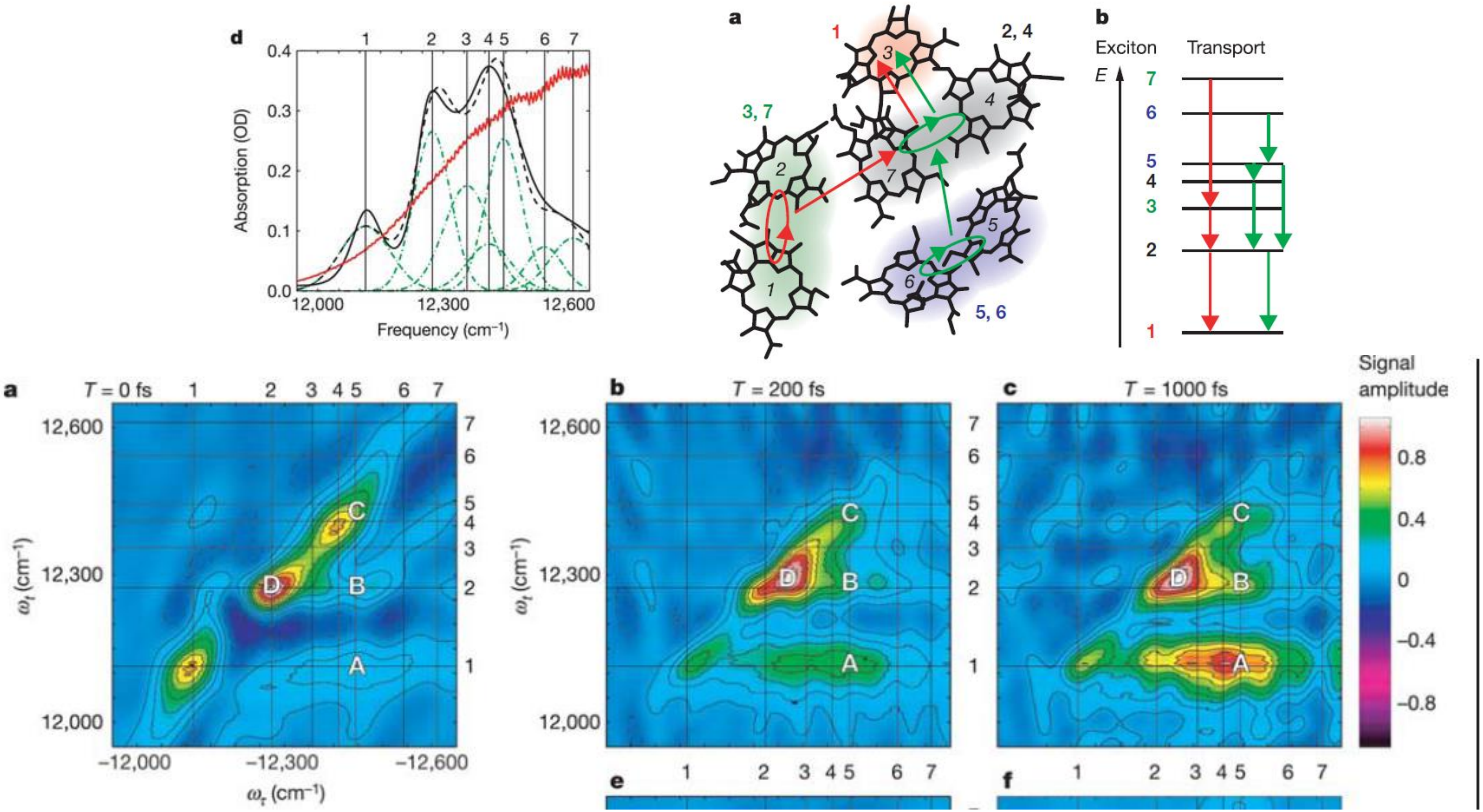
dimeric core complex

light-harvesting complexes (LHCII)

COHERENT AND INCOHERENT ENERGY TRANSFER

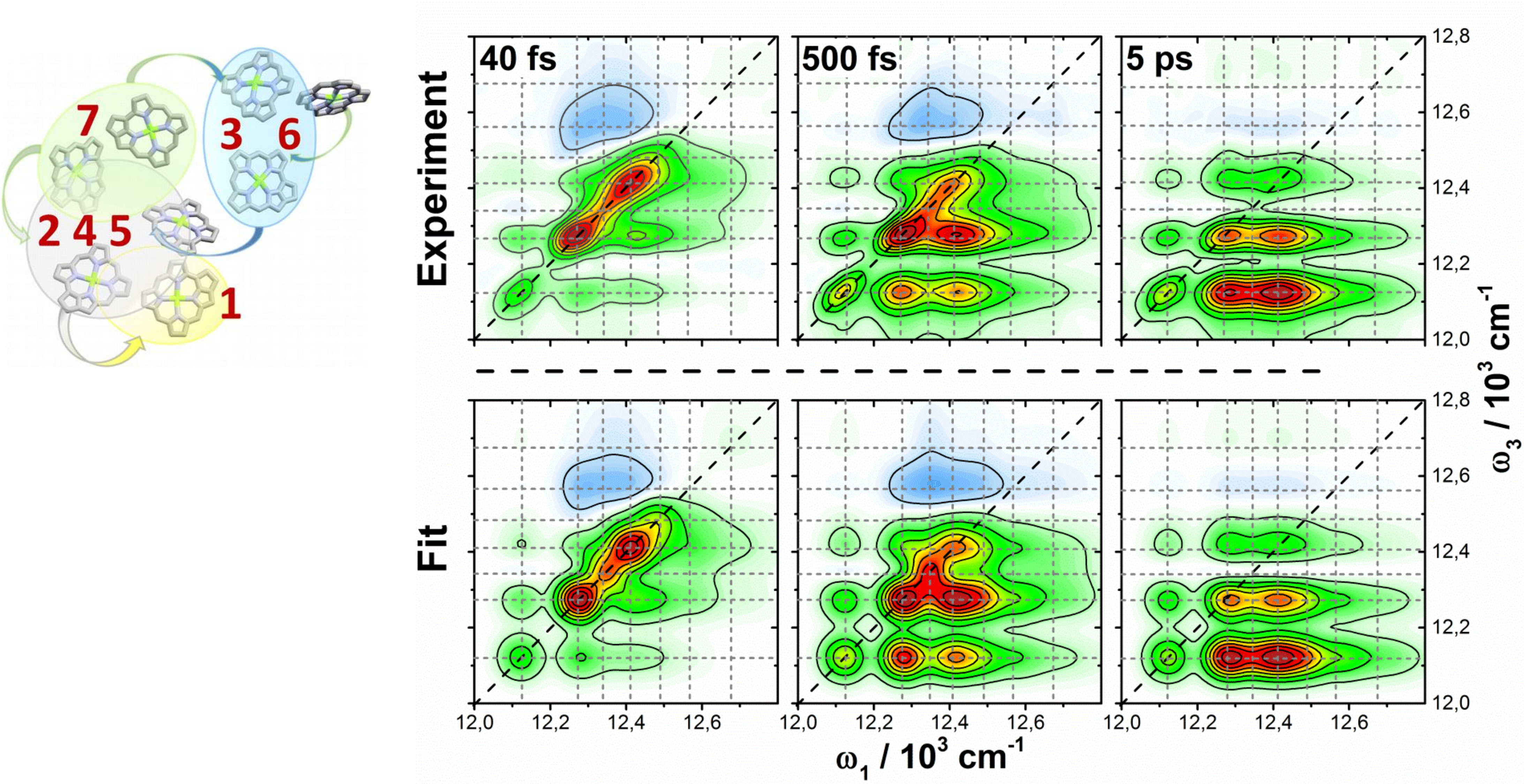


2D electronic spectroscopy of the FMO complex



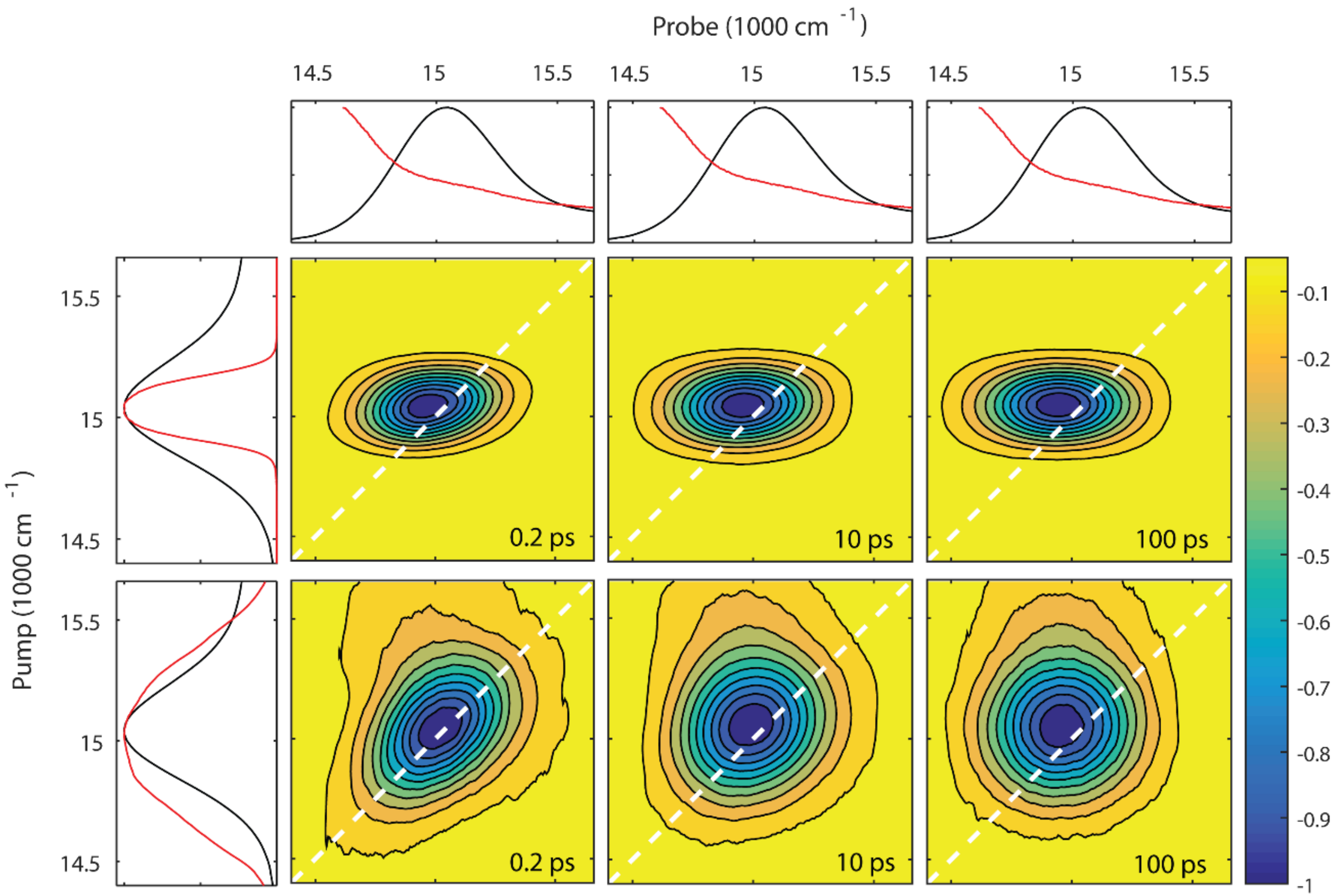
T. Brixner et. (2005) Nature

ENERGY TRANSFER IN THE FENNA-MATHEWS-OLSON COMPLEX



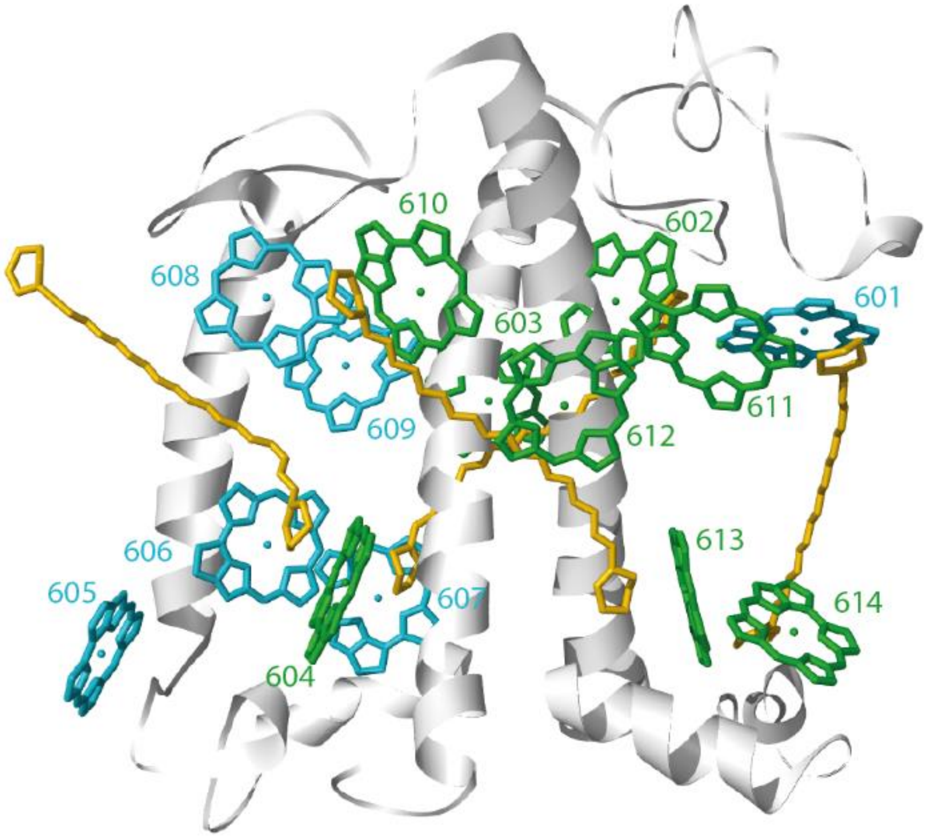
Thyrhaug *et al.* (2016) *JPCL*

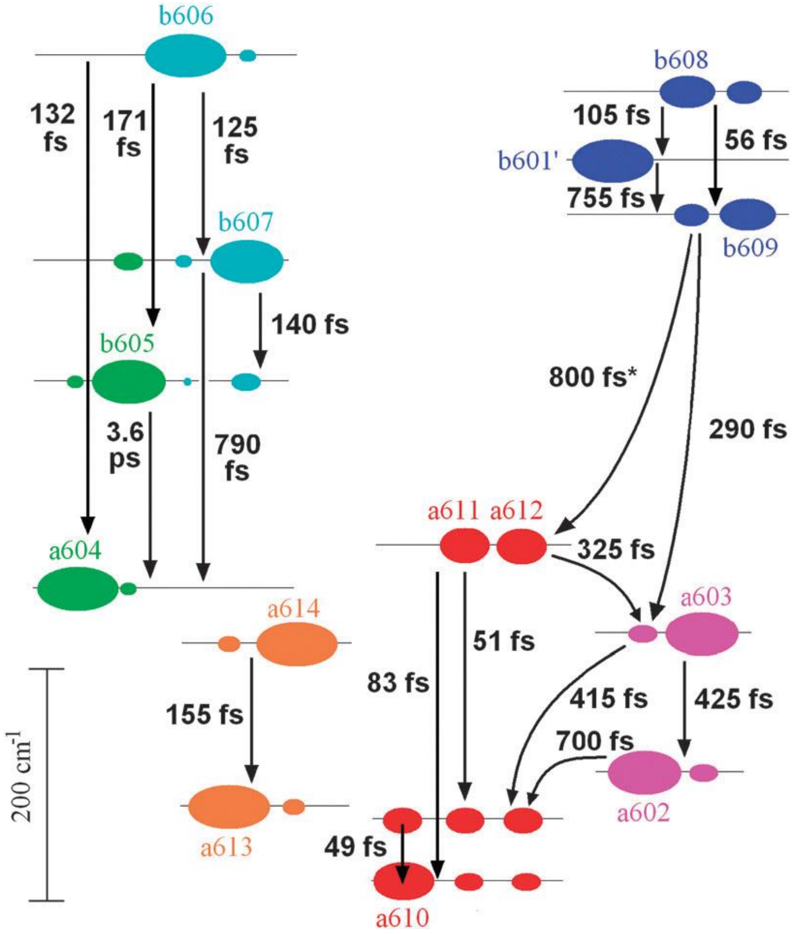
SPECTRAL DIFFUSION IN CHLOROPHYLL *A*



Nowakowski *et al.* (2018) *Chem Phys*

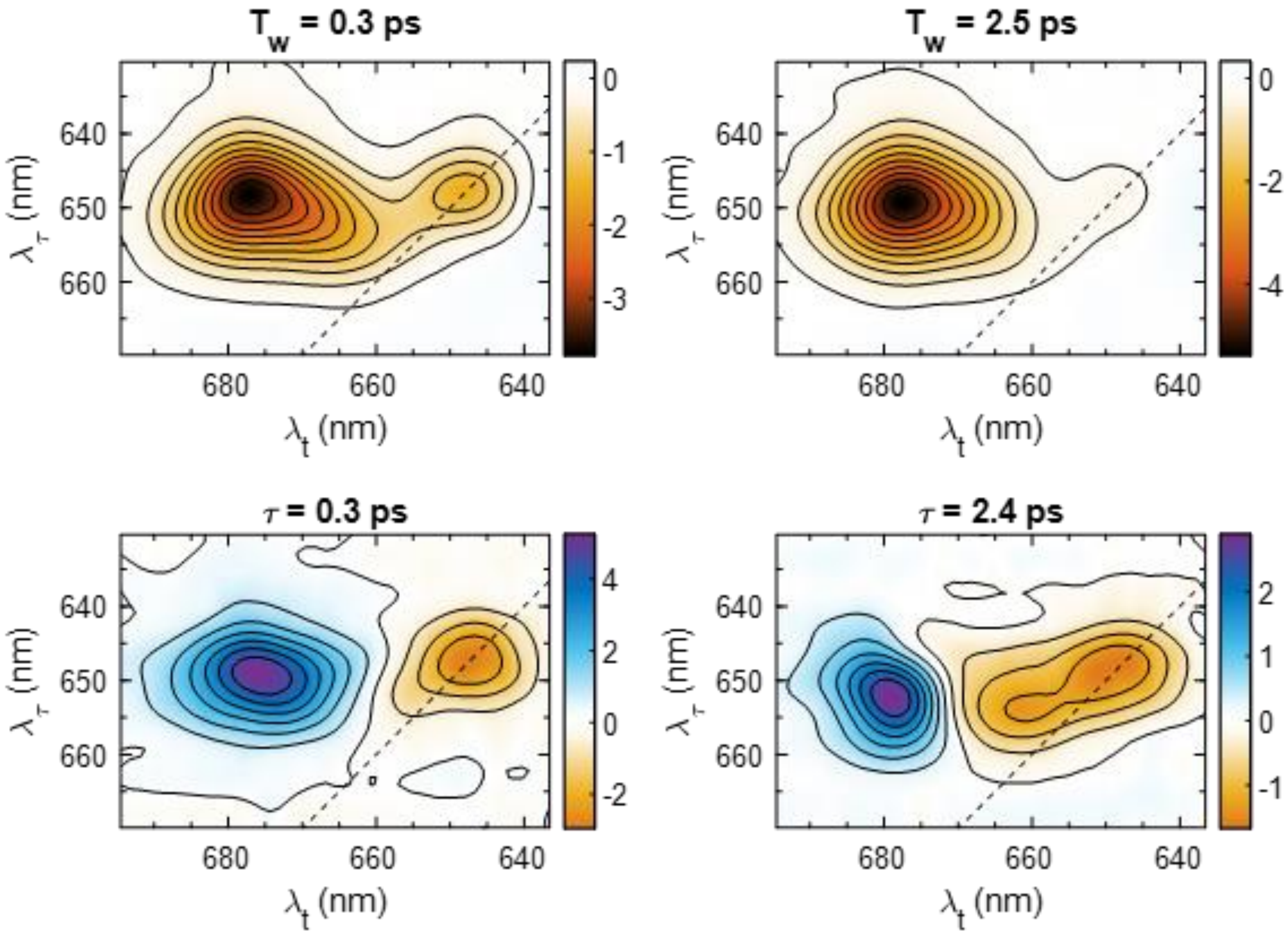
ENERGY TRANSFER IN LIGHT-HARVESTING COMPLEX II





Novoderezhkin *et al*. (2011) *PCCP*

2DES OF LHCII – CHLOROPHYLL B EXCITATION



Global lifetime analysis

$$S(\lambda_1, \lambda_3, t) = \sum_{i=1}^{n} A_i(\lambda_1, \lambda_3)\, e^{-\frac{t}{\tau}}$$

τ – lifetimes

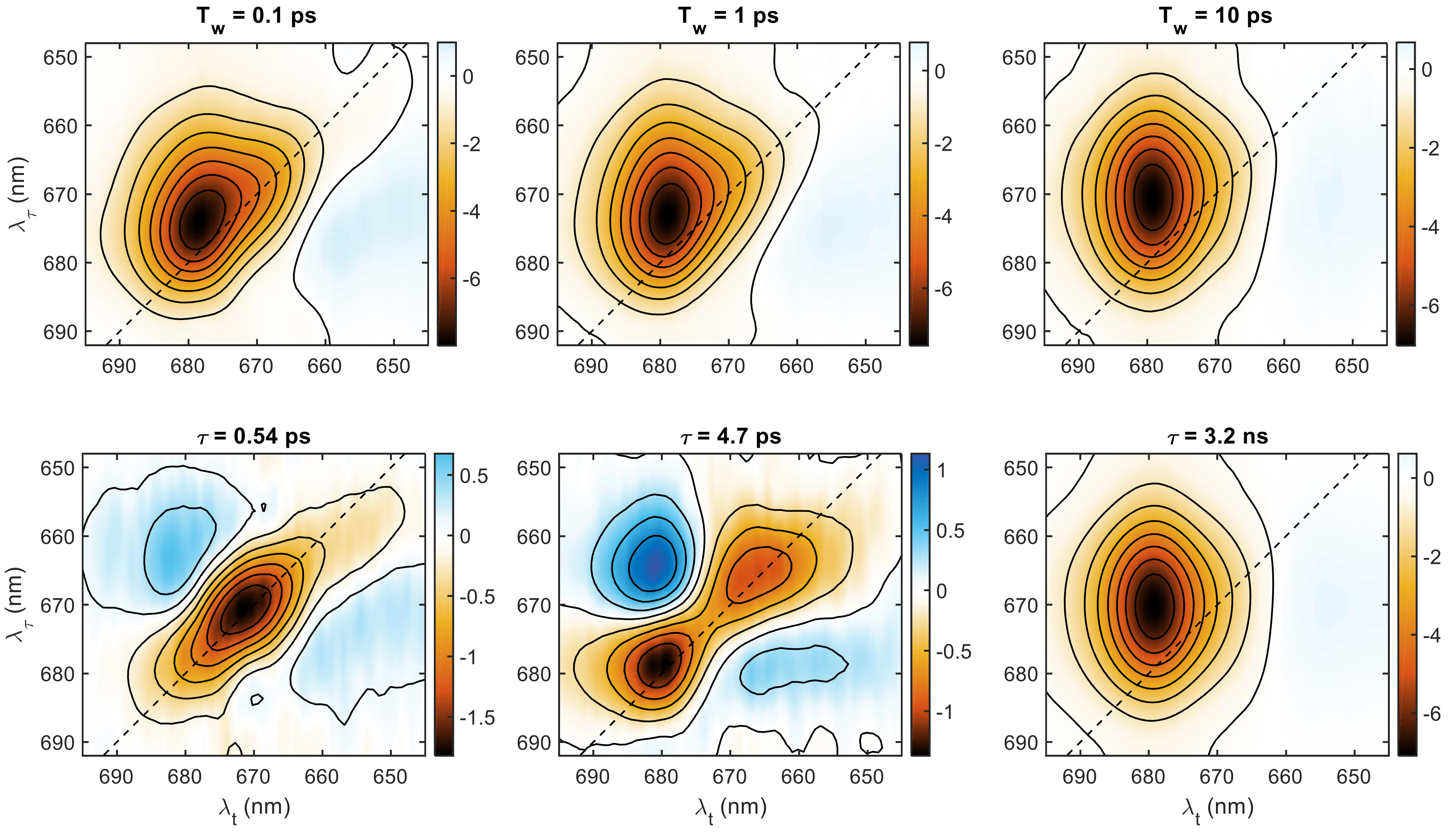
$A_i(\lambda_1, \lambda_3)$ – 2D DAS

negative peaks – population decay

positive peaks – population rise

Wells et al. (2014) PCCP

2D SPECTRA OF LHCII AT ROOM TEMPERATURE



Akhtar et al. (2017) J. Phys. Chem. Lett.

SUMMARY

2DES reveals information about:

- excitonic couplings between chromophores
- population dynamics (energy transfer) between chromophores
- coherent dynamics (exciton, vibrational and vibronic coherence)
- homogeneous and inhomogeneous broadening (energy disorder)
- dynamics of spectral diffusion
- bidirectional uphill/downhill energy transfer and thermal equilibration

BRC – ELI-ALPS COLLABORATION

NEMZETI KUTATÁSI, FEJLESZTÉSI ÉS INNOVÁCIÓS HIVATAL

2018-1.2.1-NKP-2018-00009. Development of a multifunctional femtobiology end station and study of light-driven biological processes by few-cycle based spectroscopic methods

Multidimensional Electronic Spectroscopy with Ultrashort, Ultrabroadband Pulses