2D ELECTRONIC SPECTROSCOPY

Petar Lambrev
Biological Research Centre, Szeged
2D ELECTRONIC SPECTROSCOPY FUNDAMENTALS

- 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

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

\[ E = \hbar \omega \]
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

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

Transition probability (Fermi’s Golden Rule)

\[ E_0^2 \cdot |\mathbf{E} \cdot \langle \Psi_0 | \mathbf{\mu} | \Psi_1 \rangle|^2 = |E_0|^2 \cdot |\mathbf{\mu}|^2 \cdot \cos^2(\mathbf{E} \cdot \mathbf{\mu}) \]
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

Coherent superposition of states

\[ \Psi_{01} = c_0 \Psi_0 + c_1 \Psi_1 = c_0 \psi_0 e^{-iE_0 t/\hbar} + c_1 \psi_1 e^{-iE_1 t/\hbar} \]

Oscillation frequency

\[ \omega_{01} = (E_1 - E_0)/\hbar \]
EXCITATION ENERGY TRANSFER

Förster resonance energy transfer

\[
k_{AB} = \frac{9\kappa^2 c^4}{8\pi\tau_A n^4 R^6} \int F_A(\omega)\sigma_B(\omega)\frac{d\omega}{\omega^4}
\]

Typical energy transfer times

\(10^{-14} - 10^{-9} \text{ s}\)
THE EXCITONIC DIMER

Exciton (Frenkel) Hamiltonian

\[ H = H_1 + H_2 + V \]

\[ V = \frac{1}{4\pi\varepsilon_0 r^3} (\mathbf{\mu}_1 \cdot \mathbf{r}_2 - 3(\mathbf{\mu}_1 \cdot \mathbf{r})(\mathbf{\mu}_2 \cdot \mathbf{r})) \]

\[(H_1 + H_2 + V)\Psi_\alpha = E_\alpha \Psi_\alpha \]

\[ \mathbf{H} = \begin{pmatrix} \langle \Psi_1 | H | \Psi_1 \rangle & \langle \Psi_1 | H | \Psi_2 \rangle \\ \langle \Psi_2 | H | \Psi_1 \rangle & \langle \Psi_2 | H | \Psi_2 \rangle \end{pmatrix} = \begin{pmatrix} E_1 & V \\ V & E_2 \end{pmatrix} \]

Solution – exciton states

\[ E_\alpha = E \pm V \]

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

\[ \mathbf{\mu}_\alpha = \frac{1}{\sqrt{2}} (\mathbf{\mu}_1 \pm \mathbf{\mu}_2) \]
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 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

- 'Pump' pulse creates excited states (GS→$S_1$)
- A subsequent 'probe' pulse ($S_1→S_n$) 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 $k_{sig} = k_1 - k_1 + k_2$

Differential absorption:
\[ \Delta A(t) = A_{+pump} - A_{-pump} \]
**GSB** - ground-state bleaching

**SE** - stimulated emission

**ESA** - excited-state absorption

\[ E = \hbar \omega \]
EXPERIMENTAL SETUP FOR PUMP-PROBE SPECTROSCOPY

- **Source 1**
  - Ti:sapphire
  - 800 nm, 1 kHz
  - 100 fs

- **Source 2**

- **Optical modulator**

- **Delay line (τ)**

- **Computer controlled**

- **Probe**

- **Pump**

- **Detector**

- **Sample**

- **Spectrometer**
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

\[ \tau \quad T_w \quad t \]

- \( \tau \) – coherence time
- \( T_w \) – waiting time
- \( t \) – detection time

- oscillation frequency \( \omega_\tau \)
- population transfer
- echo signal frequency \( \omega_t \)
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

Schematic 2D electronic spectrum of a coupled three-level system
2D ELECTRONIC SPECTROSCOPY – EXCITONIC COUPLING

Fassioli et al. (2014) JRS Interface
Cross peaks in the 2D spectrum reveal energy transfer
Cross-peak at \((\lambda_1 = A, \lambda_3 = B)\) reflects energy transfer from \(|a\rangle\) to \(|b\rangle\).

- \(\lambda_1 = A\) – donor’s Abs wavelength
- \(\lambda_3 = B\) – acceptor’s Abs wavelength

Cross-peak amplitude

\[
\begin{align*}
\text{Cross-peak amplitude} \\
\text{Time (ps)}
\end{align*}
\]
EXCITONIC COUPLING AND ENERGY TRANSFER

\[ T_w = 0 \]

\[ T_w > 0 \]

Oliver (2018) R Soc open sci
$$\frac{k_{ab}}{k_{ba}} = e^{-\frac{\Delta E}{k_B T}}$$

Detailed balance (Boltzmann distribution)
2D LINESHAPES

Homogeneous

Inhomogeneous

$\omega_3$  $\Omega_0$  $\Omega_0$

$\Omega_0$  $\omega_1$

$\Omega_0$
2D LINESHAPES: LOSS OF FREQUENCY CORRELATION

\[ \tau_2 \ll \tau_c \]

\[ \tau_2 \gg \tau_c \]

Ellipticity

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

**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

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Oliver (2018) R Soc open sci
PHASE MATCHING VS PHASE CYCLING

Phase matching (BOXCARS)

Phase cycling (Pump-probe geometry)

Signal at 680 nm

\[ \text{Signal at 680 nm} \]

\[ R_2, R_3, R_1, R_4 \]

rephasing

\[-k_1 + k_2 + k_3\]

non-rephasing

\[ +k_1 - k_2 + k_3\]
INTERFEROMETER-BASED BOXCARS SETUP

BOXCARS SETUP USING DIFFRACTIVE OPTICS

G. Fleming, UC Berkeley, USA
PULSE-SHAPER-ASSISTED PUMP-PROBE GEOMETRY SETUP

H.-S. Tan, NTU, Singapore
Fourier synthesis via parallel spatial/spectral modulation
Variety of spatial light modulators (SLM): LCD, LCM, deformable mirrors, AOM

Acousto-optic Programmable Dispersive Filter (AOPDF)
APPLICATIONS IN PHOTOSYNTHESIS
PHOTOSYNTHESIS POWERS LIFE

Solar energy → Oxygen

Heat losses → Higher free energy
Decreased entropy

Organic compounds → Chemotrophes

Chemical energy → Lower free energy
Increased entropy

Carbon dioxide
Nitrate
Water

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PHOTOSYNTHETIC ELECTRON TRANSPORT

1. Water (H₂O) is split by Photosystem II, producing oxygen (½O₂) and 4 protons (4H⁺).
2. 4 protons (4H⁺) are pumped into the thylakoid space, creating a proton gradient.
3. Protons (H⁺) flow through ATP synthase, producing ATP (adenosine triphosphate).

The ATP is then used in the Calvin Cycle.
CHLOROPHYLL STRUCTURE

porphyrin

chlorophyll

heme b

chlorophyll d
PHOTOCHEMISTRY OCCURS IN THE REACTION CENTRE

Photosystem II reaction centre

stroma

thylakoid space

Photosystem II reaction centre
THE PSII-LHCII SUPERCOMPLEX

Su et al. 2017 Science
Most of the chlorophylls function as light-harvesting antenna.

PDB ID: 5XNL (Su et al. 2017)
COHERENT AND INCOHERENT ENERGY TRANSFER

- Delocalization of excitation over strongly interacting Chl’s.
- Energy transfer from a molecule to another molecule
- Energy transfer by the relaxation among the excitonic states.
2D electronic spectroscopy of the FMO complex

T. Brixner et. al. (2005) Nature
ENERGY TRANSFER IN THE FENNA-MATHEWS-OLSON COMPLEX

Thyrhaug et al. (2016) JPCL
SPECTRAL DIFFUSION IN CHLOROPHYLL A

ENERGY TRANSFER IN LIGHT-HARVESTING COMPLEX II

Novoderezhkin et al. (2011) PCCP
Global lifetime analysis

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

\( \tau \) – lifetimes

\( A_i(\lambda_1, \lambda_3) \) – 2D DAS

negative peaks – population decay

positive peaks – population rise
2D SPECTRA OF LHCII AT ROOM TEMPERATURE

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
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