Coherent multidimensional spectroscopies: advanced spectroscopic techniques to unveil complex dynamics

Elisabetta Collini
elisabetta.collini@unipd.it

Femto-UP 2020-21: Ultrafast lasers technologies and applications
8-29 Mar 2021 Online (France)
11.2. COHERENT SPECTROSCOPY AND NONLINEAR POLARIZATION

We will specifically be dealing with the description of coherent nonlinear spectroscopy, which is the term used to describe the case where one or more input fields coherently act on the dipoles of the sample to generate a macroscopic oscillating polarization. This polarization acts as a source to radiate a signal that we detect in a well-defined direction. This class includes experiments such as pump-probes, transient gratings, photon echoes, and coherent Raman methods. However, understanding these experiments allows one to rather quickly generalize to other techniques.

Detection: Coherent

Dipoles are driven coherently, and radiate with constructive interference in direction $s_{\text{gik}}$. Dipoles radiate independently.

**Linear**: Absorption, Fluorescence, phosphorescence, Raman, and light scattering

**Nonlinear**: Pump-probe transient absorption, photon echoes, transient gratings, CARS, impulsive Raman scattering, Fluorescence-detected nonlinear spectroscopy, i.e. stimulated emission pumping, time-dependent Stokes shift

**Keywords**: 'coherent', 'multidimensional', 'dynamics', 'complex'
A second dimension was introduced for the first time in NMR spectroscopy,
NOESY (nuclear Overhauser enhancement spectroscopy)
COSY (correlation spectroscopy)
These technique have been extensively used to study structural and dynamical properties of proteins in solution.

In the optical regime, the origin of multidimensional vibrational spectroscopy can be traced to the coherent anti-Stokes Raman spectroscopy (CARS) measurements of vibrational dephasing performed in the 1970s.
2D vibrational spectroscopic technique (2D-IR) can provide detailed information on the 3D structure of a given complex molecule, i.e., proteins, water networks,…

2D electronic spectroscopy was introduced by Fleming Delay with respect to the IR counterpart due to experimental problems connected with the higher frequency of Visible light.
CMDS techniques can be declined at different orders of the nonlinear polarizability (3°, 5°, etc.) and in different spectral ranges (IR, Vis, UV...)

**2D electronic spectroscopy:**

- third order technique: generalized version of a 4-wave mixing spectroscopy
- in the Vis range: electronic transitions
2D electronic spectroscopy (2DES): why and when?
Conventional optical spectroscopy techniques, such as ordinary infrared, Raman, and UV-visible spectroscopies, provide a one dimensional (1D) projection of the available molecular information of a sample onto a single frequency axis. In contrast, optical multidimensional (2D, 3D) spectroscopy techniques provide a multidimensional projection of the relevant molecular motions offering dramatically more information.
why 2DES?

- Spread information along multiple dimensions
- Simultaneously frequency and time-resolved
- Couplings and transport processes mapped far from diagonal positions (where main dynamical processes take place)
- Sensitivity to coherent dynamic mechanisms (oscillations)

Why not?
- complex (and expensive) optical setups
- demanding data processing and analysis
- challenging interpretation of the data (artefacts)

ideal to untangle complex dynamics (transport processes) in complex multichromophore systems
biological antennas

strongly coupled J-aggregates

porphyrin-peptide self assemblies

porphyrin functionalized oligomers

rhodamine dimers on DNA

transport in QDs materials

hybrid metal-organic nanomaterials

JPCLett11(2020)7972

PCCP22(2020)7516

JPCLett11(2020)1059

NatureComm9(2018)3160

JPCLett7(2016)4996

JPCC123(2019)10212

JPCC124(2020)16222

JPCC123(2019)31286

JCP154(2021)014301

Nanoscale(2021) 10.1039/D1NR00775K
2D electronic spectroscopy: the experiment
A real example

2DES setup
The heterodyne signal is linear rather than quadratic in the (weak) signal field.

By controlling the relative phase of $E_{LO}$ and $E_S$ it is possible to probe separately the real and imaginary part $\Rightarrow$ phase sensitive detection.
From interferograms to 2D spectra

\[ I(\omega) = 2\text{Re}\left[ E_{LO}^{*}(\omega) \cdot E_{S}(\omega) \cdot e^{-i\omega\Delta\tau} \right] \]

\[ E_{S}(\omega) = \frac{\text{FFT}\left[ \theta(t) \text{IFFT}\{I(\omega)\}\right] e^{-i\omega\Delta\tau} \cdot E_{LO}^{*}(\omega)}{E_{LO}^{*}(\omega)} \]

CCD pixel

- \( t_1 \) (fs)
- \( \omega_1 \) (fs)
- \( \omega_3 \) (fs)

FFT
From interferograms to 2D spectra
Response Function Formalism
time-resolved non-linear techniques

Time-resolved techniques

In the **perturbative approach**, the signal is proportional to the polarization $P(r,t)$, induced in the sample by the interaction with electric fields, expressed as convolution between the fields and with the molecular response function $R^{(n)}$:

$$P_{i}^{(n)}(t) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dt_{1} dt_{2} ... dt_{n} R_{ijk...l}^{(n)}(t - t_{1}, t - t_{2}, ..., t - t_{n}) \times$$

$$E_{j}(t_{1})E_{k}(t_{2})...E_{l}(t_{n})$$

S. Mukamel, ‘Principles of nonlinear optical spectroscopy’
The susceptibility $\chi^{(n)}(\omega_1 \cdots \omega_n)$ is the Fourier-Laplace transform of the response function $R_i^{(n)}(t_1 \cdots t_n)$. 

The susceptibility $P_i^{(n)}(t) = \int \int \cdots \int d\omega_1 d\omega_2 \cdots d\omega_n \chi^{(n)}_{ijk \cdots l}(\omega_1, \omega_2, \ldots, \omega_n) \times$ 

$E_j(\omega_1)E_k(\omega_2)\cdots E_l(\omega_n) \exp[-i(\omega_1 + \omega_2 + \ldots + \omega_n)t]$ 

$\chi^{(n)}(\omega_1 \cdots \omega_n) = \int \int \cdots \int dt_1 \cdots dt_n R_i^{(n)}(t_1 \cdots t_n) \exp\left(-i \sum_{j=1}^{n} \omega_j t_j\right)$
The most general time-resolved experiment related to $P^{(3)}$ requires the interaction with 3 fields and it can be generally indicated as **four wave mixing**. In the impulsive limit (very short pulses) the signal is directly related to the response function $R^{(3)}$.

It is possible to change the relative time ordering and the phase-matching of the 3 interactions: in this way the signal becomes sensitive only to specific processes, and different techniques may be distinguished (pump&probe, photon echo, transient grating, hole burning,...)

\[
P^{(3)}_i(t) = \int \int \int_{-\infty}^{+\infty} dt_1 dt_2 dt_3 R^{(3)}_{ijk}(t - t_1, t - t_2, t - t_3) \times E_1(t_1)E_2(t_2)E_3(t_3)
\]
4-wave mixing: overview

\[ R_{ijk}^{(3)}(t-t_1, t-t_2, t-t_3) = \sum_{\alpha} R_{\alpha}^{(3)}(t-t_1, t-t_2, t-t_3) \]

\( R^{(3)} \) can be calculated within the **perturbation theory** framework using **Feynmann diagrams**. Depending on the pulse order and on the phase matching conditions, only selected diagrams (=evolution pathways along the **density matrix**) will be relevant and this simplify the calculation of the signal.

**density matrix**

\[ \rho(t) \equiv |\psi(t)\rangle \langle \psi(t)|. \]

\[ \langle A \rangle = \langle \psi | A | \psi \rangle = Tr[A\rho]. \]

\[
\begin{bmatrix}
1 & 0 \\
0 & 0
\end{bmatrix}
\]

The system is described by \( \psi_a \) (only the \( a \) state is populated)

\[
\begin{bmatrix}
\frac{1}{2} & \frac{1}{2} \\
\frac{1}{2} & \frac{1}{2}
\end{bmatrix}
\]

The system is described by a coherent superposition of \( a \) and \( b \) states:

\[
\frac{1}{2} \psi_a + \frac{1}{2} \psi_b
\]
Feynman diagram

Liouville diagram

levels diagram
output signal in 2DES \( \propto P^{(3)} \)

\( P^{(3)} \) as convolution of \( R^{(3)} \) with the exciting pulses

\( R^{(3)} \) as sum of different dynamic contributions

each contribution can be mapped into a signal at specific coordinates in the 2D map
2D electronic spectroscopy: qualitative description of the response
2DES: off-diagonal cross-peaks resolve couplings between states
2D maps

\[ R_{ijk}(t-t_1, t-t_2, t-t_3) = \sum_{\alpha} R_{\alpha}^{(3)}(t-t_1, t-t_2, t-t_3) \]

@ a fixed value of \( t_2 \)

Excited State Absorption

Negatively Correlated Spectral Motion
\[ \langle \delta \omega_j \delta \omega_k \rangle < 0 \]

Positively Correlated Spectral Motion
\[ \langle \delta \omega_j \delta \omega_k \rangle > 0 \]

Inhomogeneously Broadened Peak

Homogeneously Broadened Peak

Homogeneous Linewidth

Inhomogeneous Linewidth
2DES: off-diagonal cross-peaks resolve couplings between states
2DES: off-diagonal cross-peaks resolve couplings between states

A system that produces multiple diagonal peaks but no cross-peaks can be modeled as a set of isolated non-interacting two-level systems.
The cross-peaks at coordinates \((\omega_c, \omega_b)\) and \((\omega_c, \omega_a)\) appearing at \(t_2 > 0\) indicate that state \(c\) is coupled via energy transfer with states \(a\) and \(b\) (Forster energy transfer, FRET). No coupling between states \(a\) and \(b\) because no cross peak appears at \((\omega_b, \omega_a)\).
In the presence of resonance interactions between the two states, symmetric above and below diagonal cross-peaks appear already at $t_2=0$: the system can be modeled as a molecular (excitonic) dimer.
A dark state ($\omega_a$) can be characterized by the coupling with a bright state ($\omega_c$) in excited state absorption processes.
The diagonal section corresponds to linear spectrum.

diagonal peaks
↓
absorption peaks

2D maps (1)
Shape of the 2D spectrum reveals distribution of the environments.

Inhomogeneous broadening: diagonal peak width

Homogeneous width: anti-diagonal peak width
If we integrate the 2D map along the $\omega_{\text{exc}}$ dimension we obtain a response equivalent to pump-probe.
time evolution
coherence and population dynamics

\[
\psi(t) = c_a |\psi_a(t)\rangle + c_b |\psi_b(t)\rangle = c_a |\phi_a\rangle e^{-i\omega_a t} + c_b |\phi_b\rangle e^{-i\omega_b t}
\]

\[
P(t) = |\psi(t)|^2 \propto \cos(\omega_a - \omega_b) t
\]
3DES

Fourier maps
applications: photosynthetic antennas
a fascinating (and still debated!) hypothesis: ‘wavelike’ EET

LETTERS

Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems

Gregory S. Engel\textsuperscript{1,2}, Tessa R. Calhoun\textsuperscript{1,2}, Elizabeth L. Read\textsuperscript{1,2}, Tae-Kyu Ahn\textsuperscript{1,2}, Tomáš Mančal\textsuperscript{1,2,†}, Yuan-Chung Cheng\textsuperscript{1,2}, Robert E. Blankenship\textsuperscript{3,4} & Graham R. Fleming\textsuperscript{1,2}
overview of biological antennas

FMO (green sulfur bacteria)

2DES provided a complete picture on how the energy transfer cascade evolves from the light harvesting antenna complex to the reaction center.

It was possible to track the step-by-step energy flow through the entire unit and observed for the first time that the FMO complex serves as energy conduit between the chlorosome and the RC.
By exciting in the visible range and detecting over both visible and near-IR ranges (2-colors 2DES), it was possible to follow all the photoinduced processes:

i) the Spx internal conversion,

ii) the BChl Qx → Qy internal conversion,

iii) the Spx → B890 EET process

by tracking the formation of several cross-peaks in the 2DES maps.
lutein 2 provides a nexus for light harvesting, collecting energy from higher-lying states and funneling it downhill, partially via a debated dark state observed exclusively on lutein 2.

These results show that the protein pocket can tune Car electronic structure via tuning the geometry, a mechanism by which plants control the photophysics of solar energy capture.
This is important information in current efforts to evaluate possible opportunities to harness coherence to realize, control, and/or drive energy transduction.

complete mapping of the multiple pathways mechanism of energy flow in PCP, and the relative time constants.

the evolution of the coherence effectively moves the population on the \( Q_y \) state: the presence of coherence appears functional to the energy distribution in PCP!
applications:
quantum dots
QDs: isolated dots in solution

CdSe quantum dots (QDs)

Versatile systems:
photophysical properties tuned modulating size and ligands/solvent

Desired properties:
Stable, processable, dense manifold of states
core/shell CdSe/ZnS QDs

« 2D electronic spectroscopy techniques can successfully and efficiently dispel the intertwined dynamics of fast and ultrafast recombination processes in nanomaterials.

Hence, we propose this analysis scheme to be used in future research on novel quantum confined systems »
2DES is sensitive to FINE STRUCTURE of QDs through the detection of the evolution of superposition of electronic states

Signatures of intra-dot coherences evolution

CY Wong et al., J. Luminescence, 131 366-374, 2011

dimers of QDs in solution and solid state. The coupling between dots is modulated through the length of the coupling ligand (di-thiol)

Interest: interacting QDs with delocalized wavefunctions and engineered coherences for applications in quantum technologies
Simulations suggested important guidelines for the design of materials with wanted coherent properties:

- Short distance
- Small size
- Limited size distribution (5% optimal)
QDs dimers: inter-dot coherences

JCP 2020, accepted for publication

\[ \text{computed} \]

\[ \text{experimental} \]
applications:
working devices
action-based techniques

collinear setup (exciting pulses propagate along the same direction)

a fourth pulse is added to the pulse sequence to drive the system into an excited or ground state population.

phase modulation or phase cycling schemes: the phases of the excitation pulses are independently varied by controlled amounts; the excited state population is also modulated, and then it can be read out by some other means, for example, photocurrent or photoluminescence.

Possibility for mass spectrometry detection (and many others detection schemes!) and single molecules implementations
sub-picosecond evolution of two-dimensional spectra consistent with multiple exciton generation

selective spectroscopic information about the coherences and populations that contribute to the final observable, which can be important to understand how and which electronically excited material states are most relevant to the function of an optical or optoelectronic device.