International Workshop on Organic Matter Spectroscopy 2013
Organized by Université du Sud Toulon-Var and Aix-Marseille Université
16-19th July 2013, La Garde City, France
woms13.univ-tln.fr

FLUOROPOLE

Picosecond tunable laser

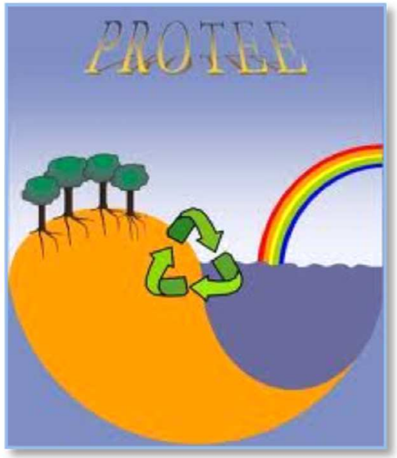
Fluorescence lifetime measurement

PROTEE Laboratory

protee.univ-tln.fr

PROTEE

- PROTEE laboratory (Processus of Transfer and Exchange in the Environment) is consisting of 4 research teams:



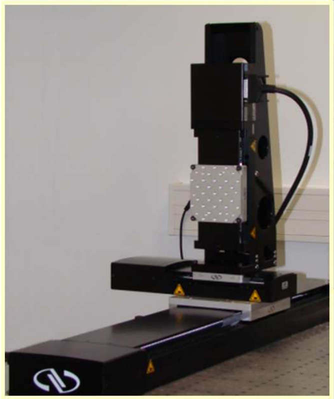
  - CAPTE: Analytical Chemistry Applied to Environmental Transfer
  - EBMA: Aquatic Environments Biology
  - EB2M: Marine Molecular Biology
  - ISO: Instrumentation, Spectroscopy and Optics

- Research topic of CAPTE & ISO: Induced fluorescence
- Fluoropole
  - Scientific facility dedicated to environment study

FLUOROPOLE

- Time Resolved Laser Spectroscopy (TRLS)

Picosecond tunable laser



High-Performance Long-Travel Linear Stages

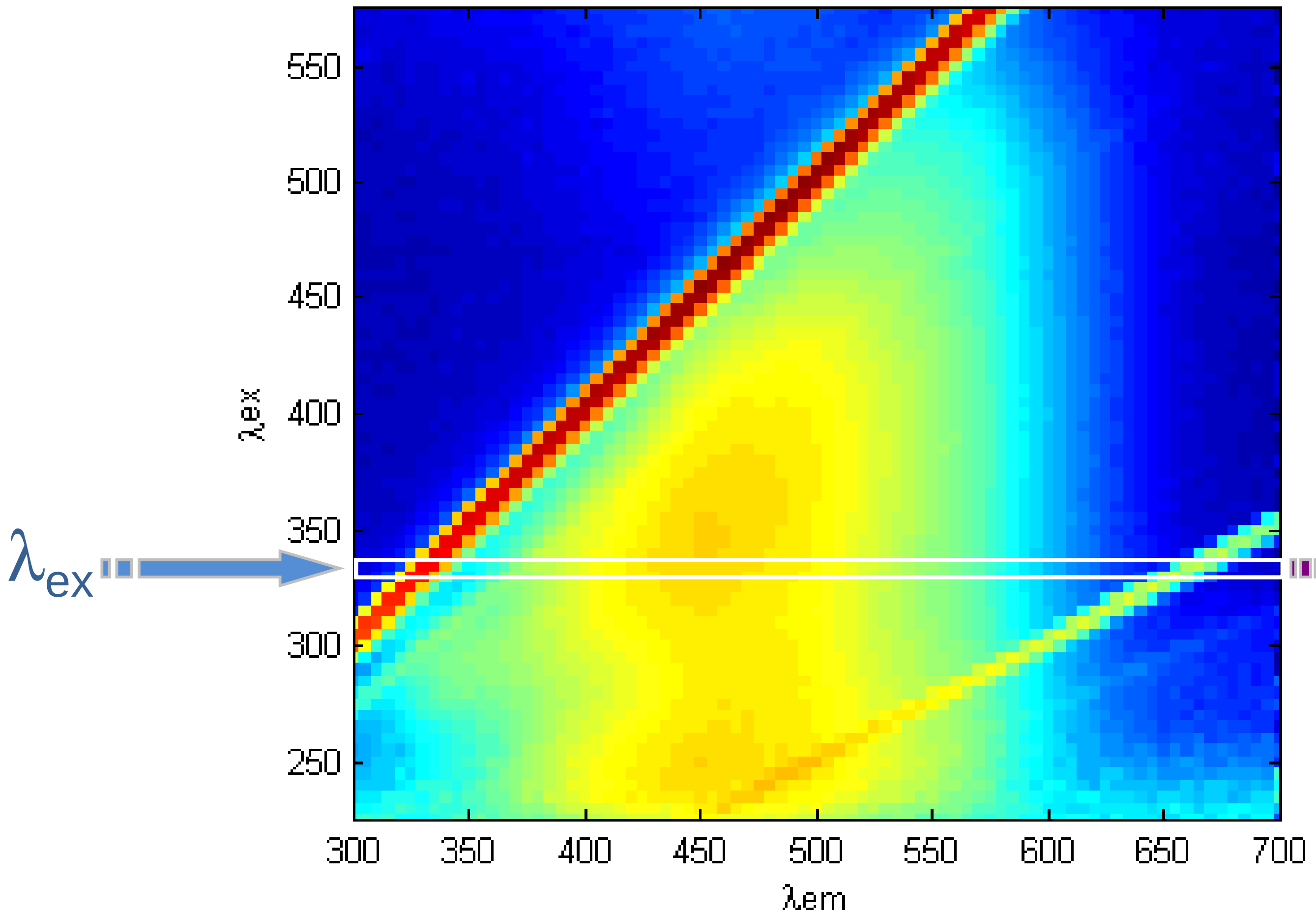
ICCD and spectrometer

- Spectrofluorimetry

Spectrofluorometer

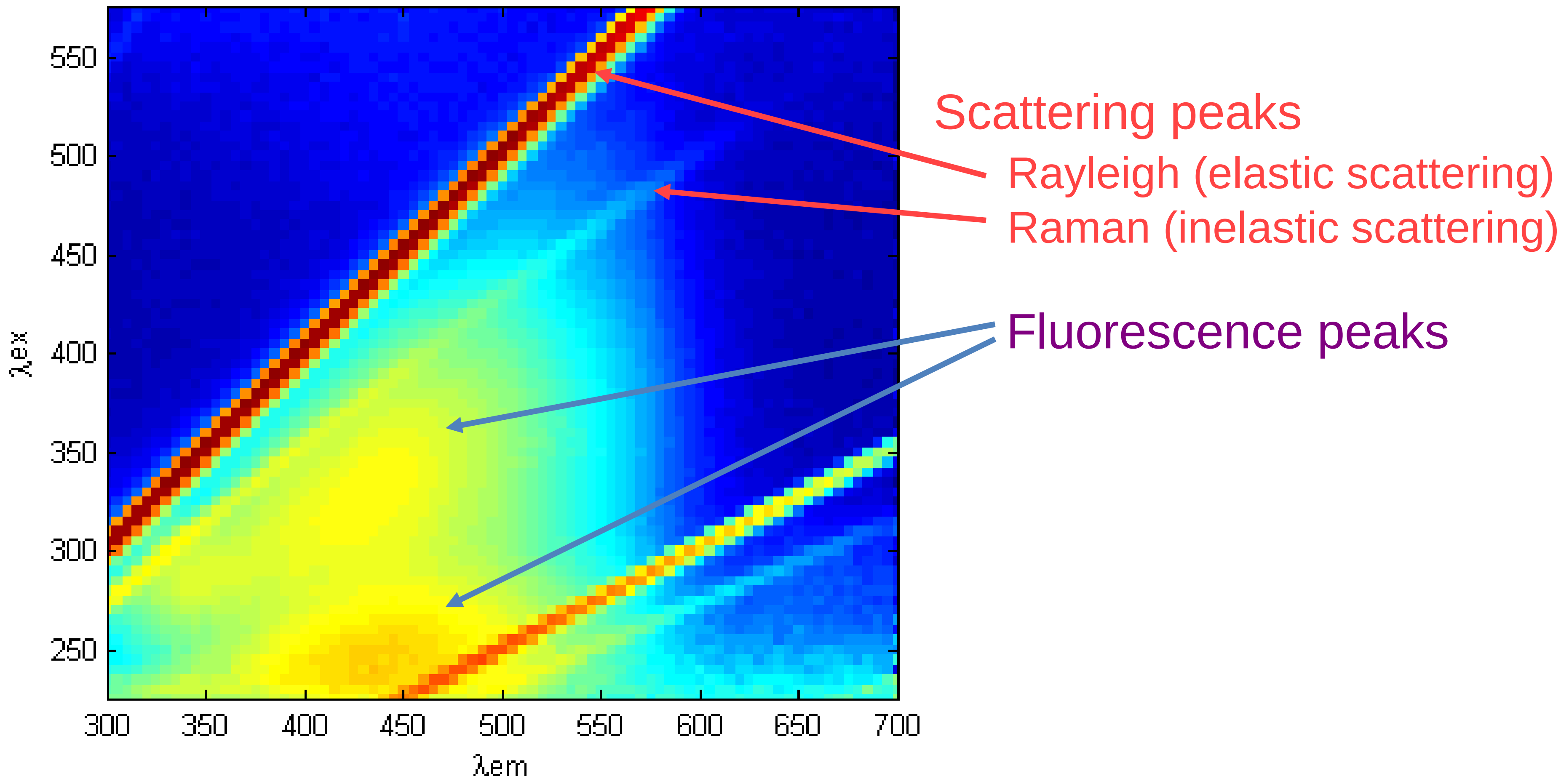
SPECTROFLUORIMETRY

- Excitation-Emission Matrix (EEM)



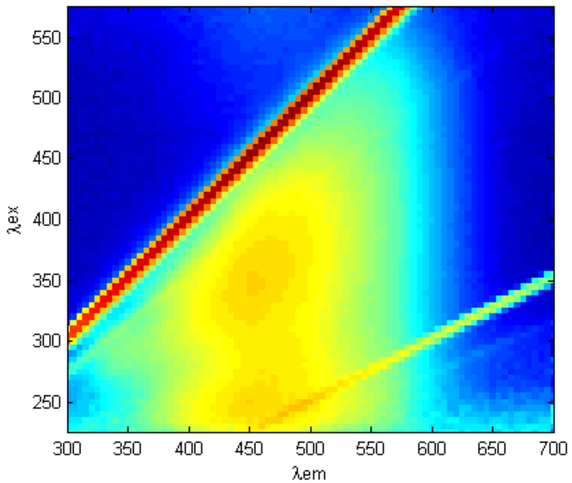
SPECTROFLUORIMETRY

- Excitation-Emission Matrix (EEM)
  - Spectral contributions



SPECTROFLUORIMETRY

- Trilinear model
  - For the k-th sample compounded of N fluorophores, fluorescence intensity $x_k(\lambda_{ex},\lambda_{em})$ is given by:

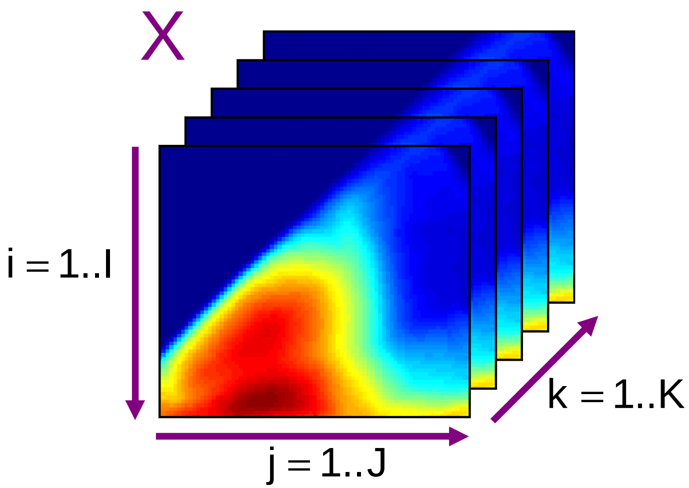


$$x_k\left(\lambda_{ex},\lambda_{em}\right) = \sum_{n=1}^{N} c_{kn}\,\phi_n\,\varepsilon_n\left(\lambda_{ex}\right)\gamma_n\left(\lambda_{em}\right)$$

- c_{kn}: concentration of the fluorophore n
- ϕ_n: quantum yield of fluorescence
- ε_n: molecular absorption coefficient
- γ_n: emission spectrum of fluorophore n

SPECTROFLUORIMETRY

- Trilinear model
  - Each measured value $\mathbf{x_{i,j,k}}$ is only depending on three vectors $\mathbf{a_{i.}}$, $\mathbf{b_{j.}}$ and $\mathbf{c_{k.}}$:



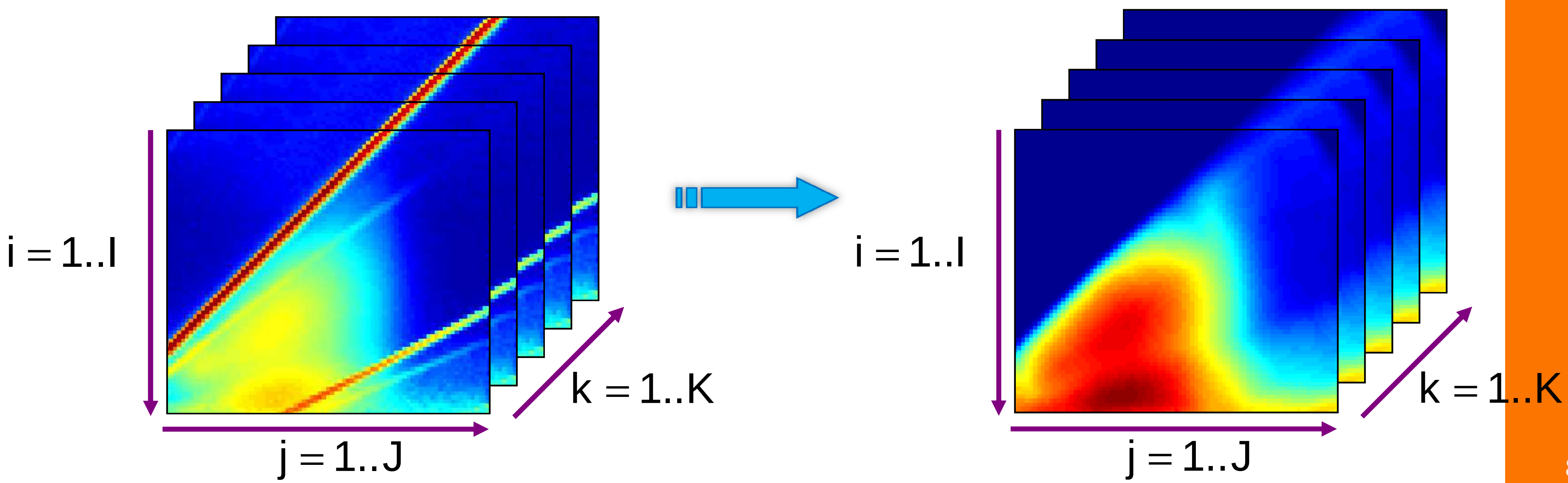
$$x_{i,j,k} = \sum_{n=1}^{N} a_{in}\, b_{jn}\, c_{kn}$$
$$where\ i \in [1, I],\ j \in [1, J]\ and\ k \in [1, K]$$

  - In the general case, the trilinear model is defined by:

$$x_{i,j,k} = \sum_{n=1}^{N} a_{in}\, b_{jn}\, c_{kn} + e_{i,j,k}$$

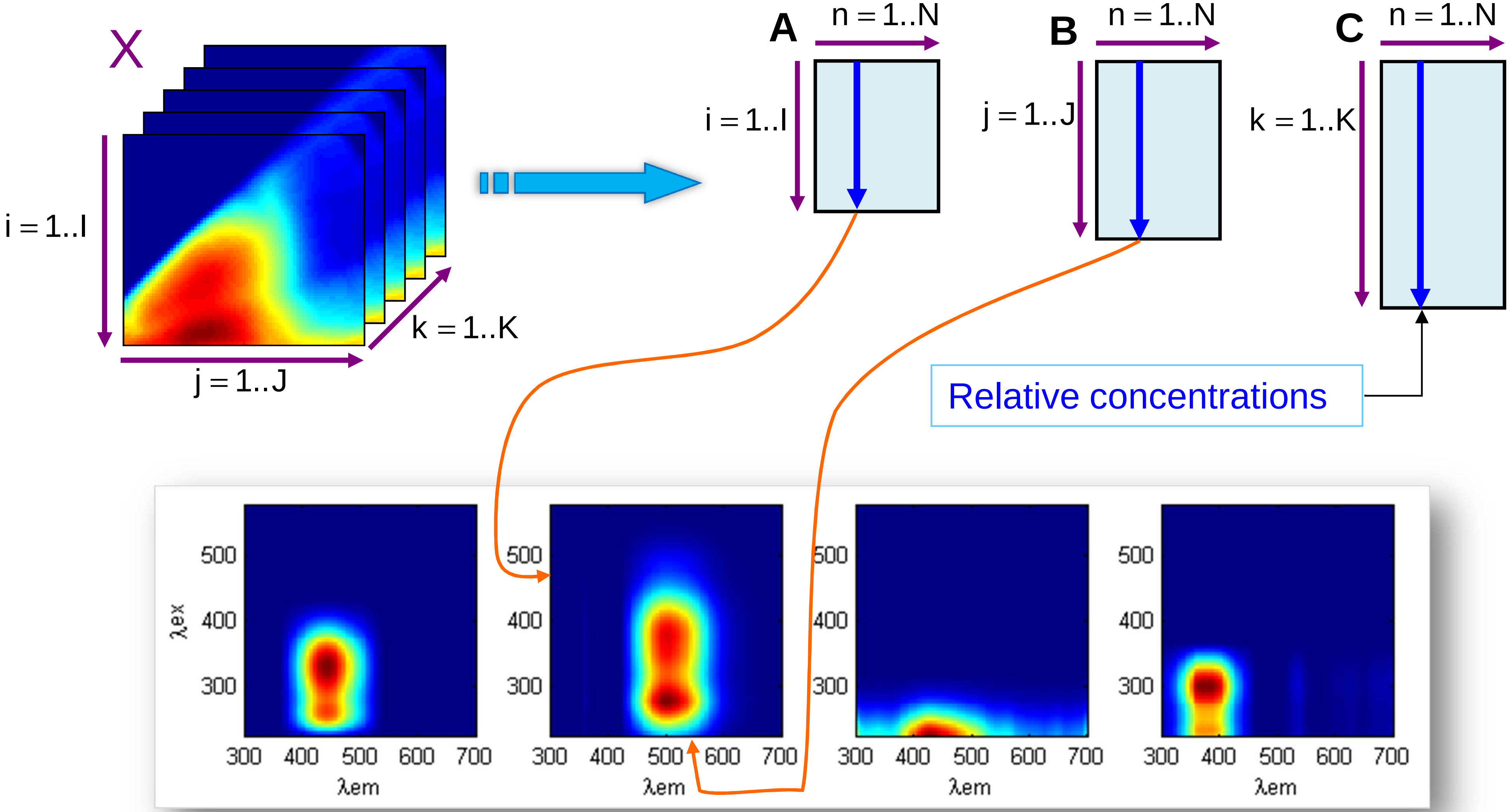
SPECTROFLUORIMETRY

- Pretreatment
  - The measured EEMs do not follow the trilinear model because Rayleigh and Raman scattering phenomena.
  - It is thus necessary to suppress these signals using a specific numerical treatment.



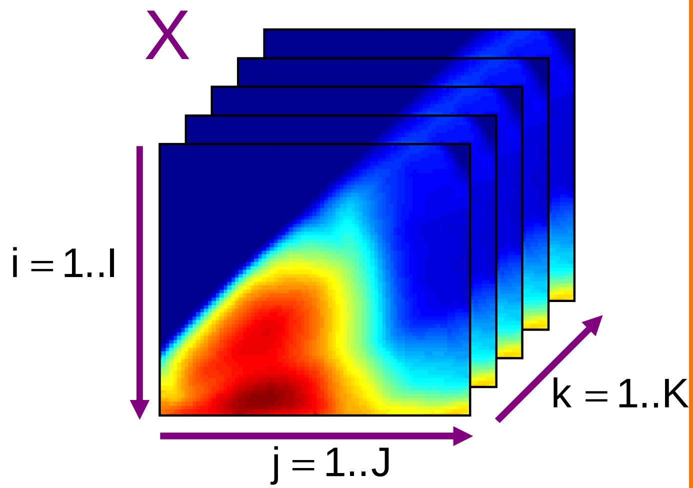
SPECTROFLUORIMETRY

- Trilinear decomposition



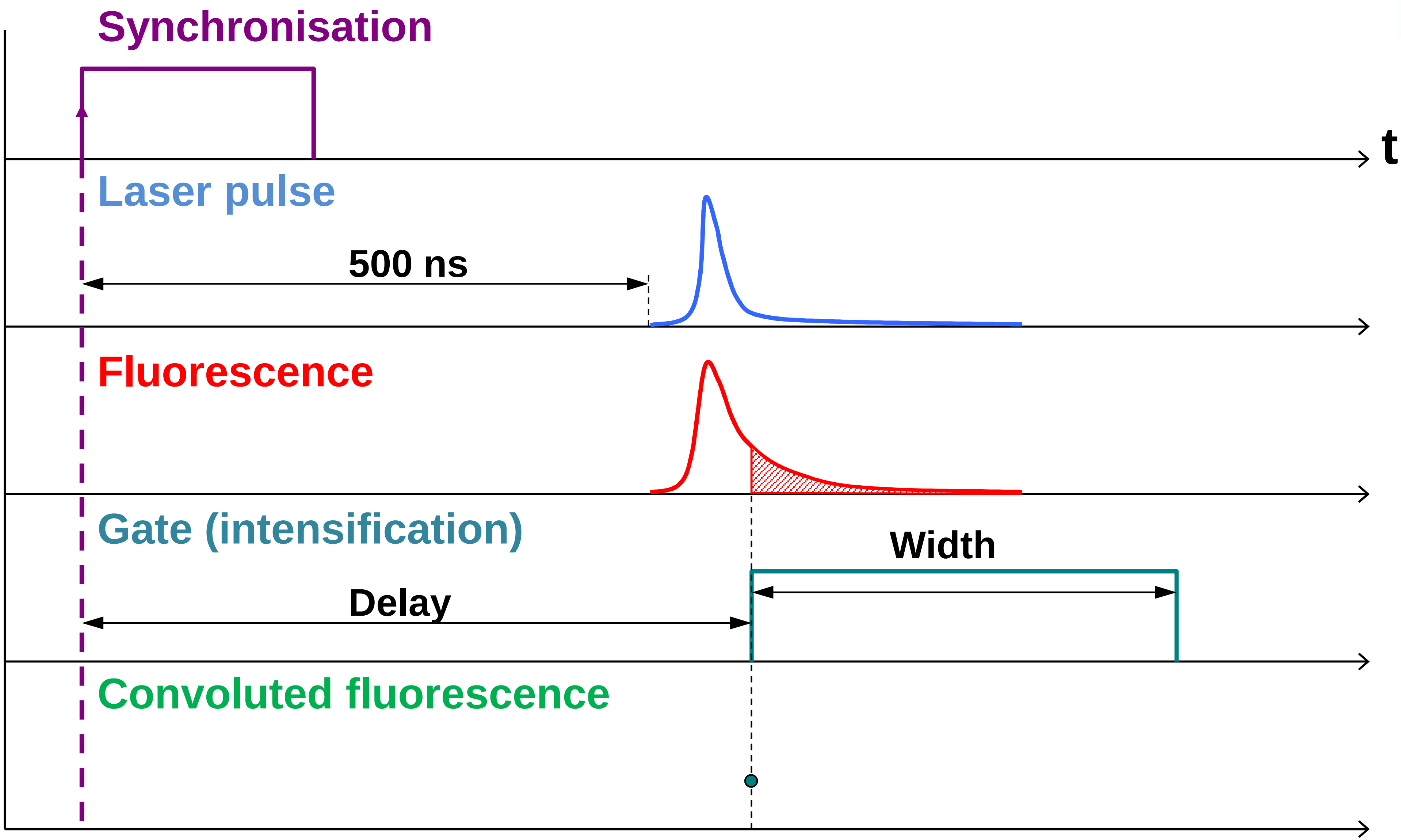
SPECTRAL CONTRIBUTIONS

- Spectrofluorimetry
  - Requires K samples
  - Continuous light excitation
  - *Spectral contributions*



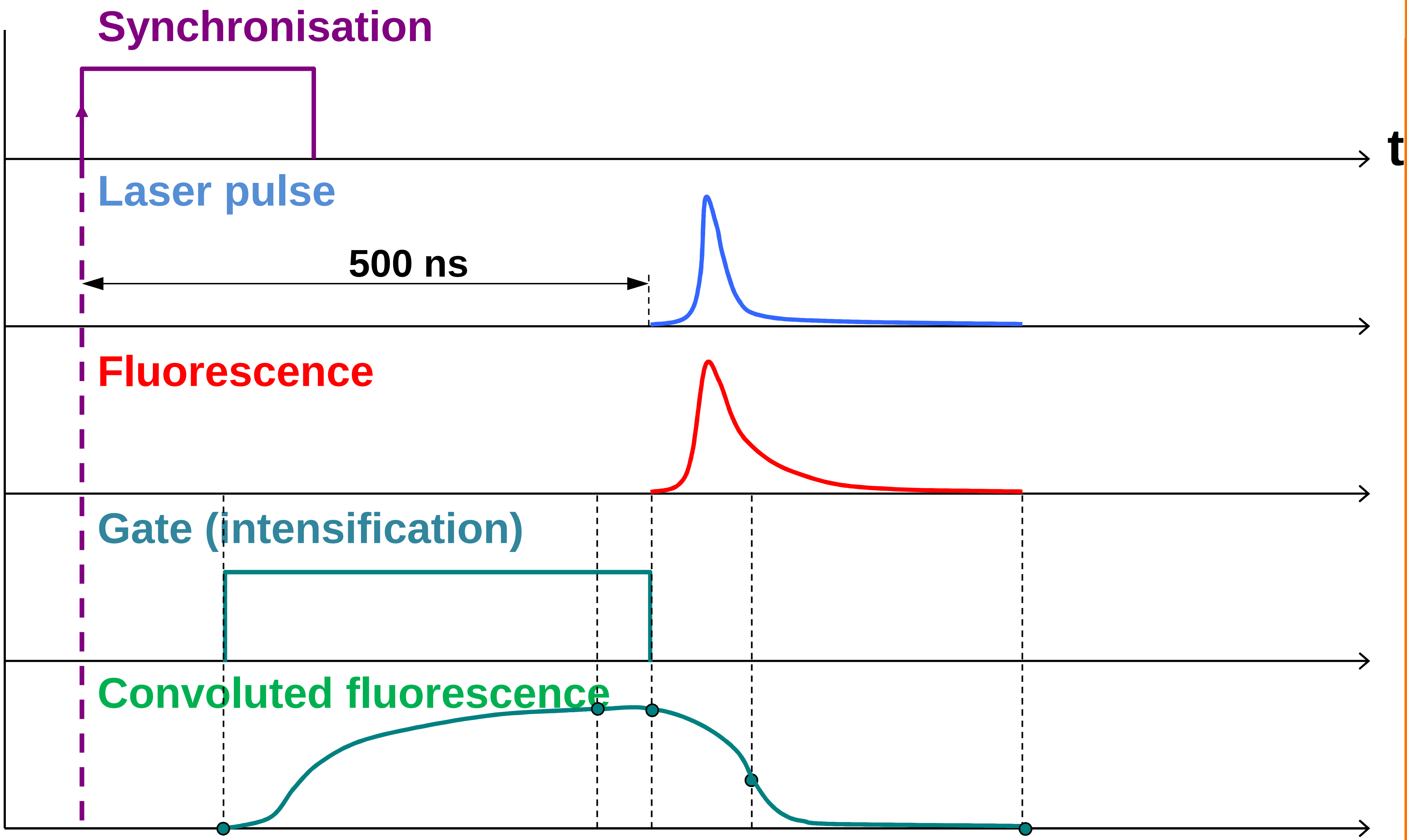
- Time Resolved Laser Spectroscopy
  - Requires one sample
  - Laser pulse
  - *Spectral contributions*
  - *Lifetime associated to each spectral contribution*

TIME RESOLVED LASER SPECTROSCOPY



For a given emission wavelength λ_{em}

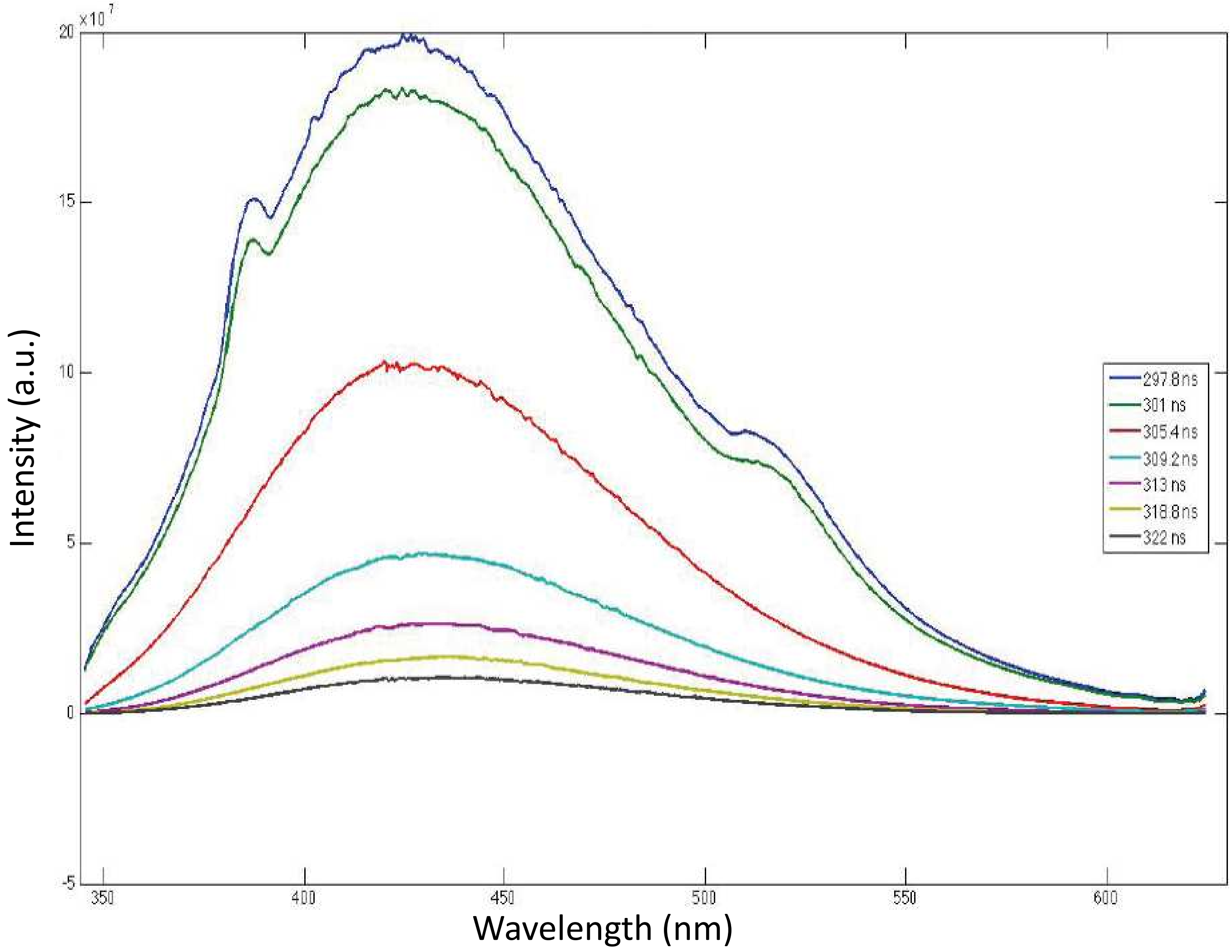
TIME RESOLVED LASER SPECTROSCOPY



For a given emission wavelength λ_{em}

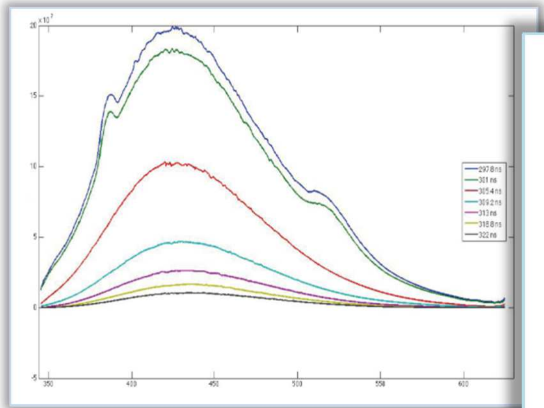
TIME RESOLVED LASER SPECTROSCOPY

- Emission spectra obtained for different delays

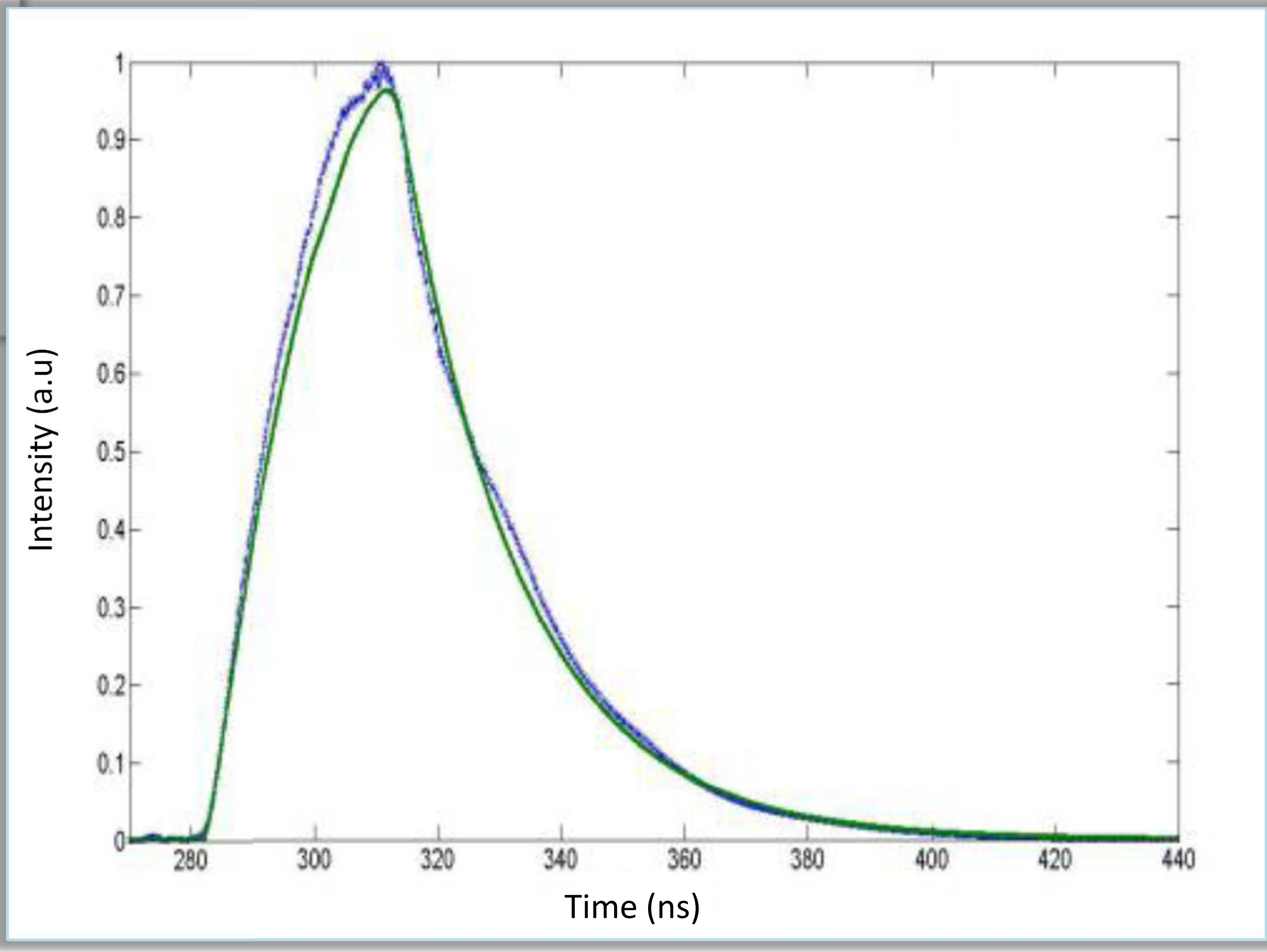


TIME RESOLVED LASER SPECTROSCOPY

- Time evolution of fluorescence intensity

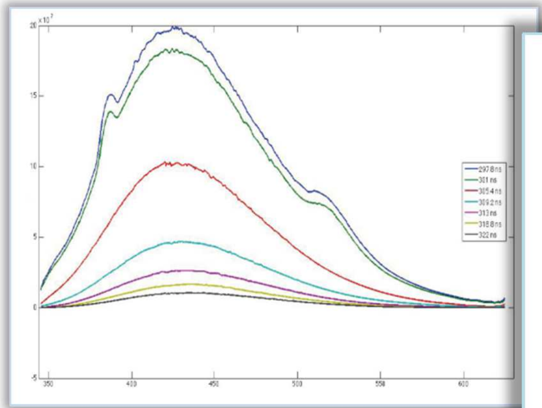


$$\int_{\lambda}$$

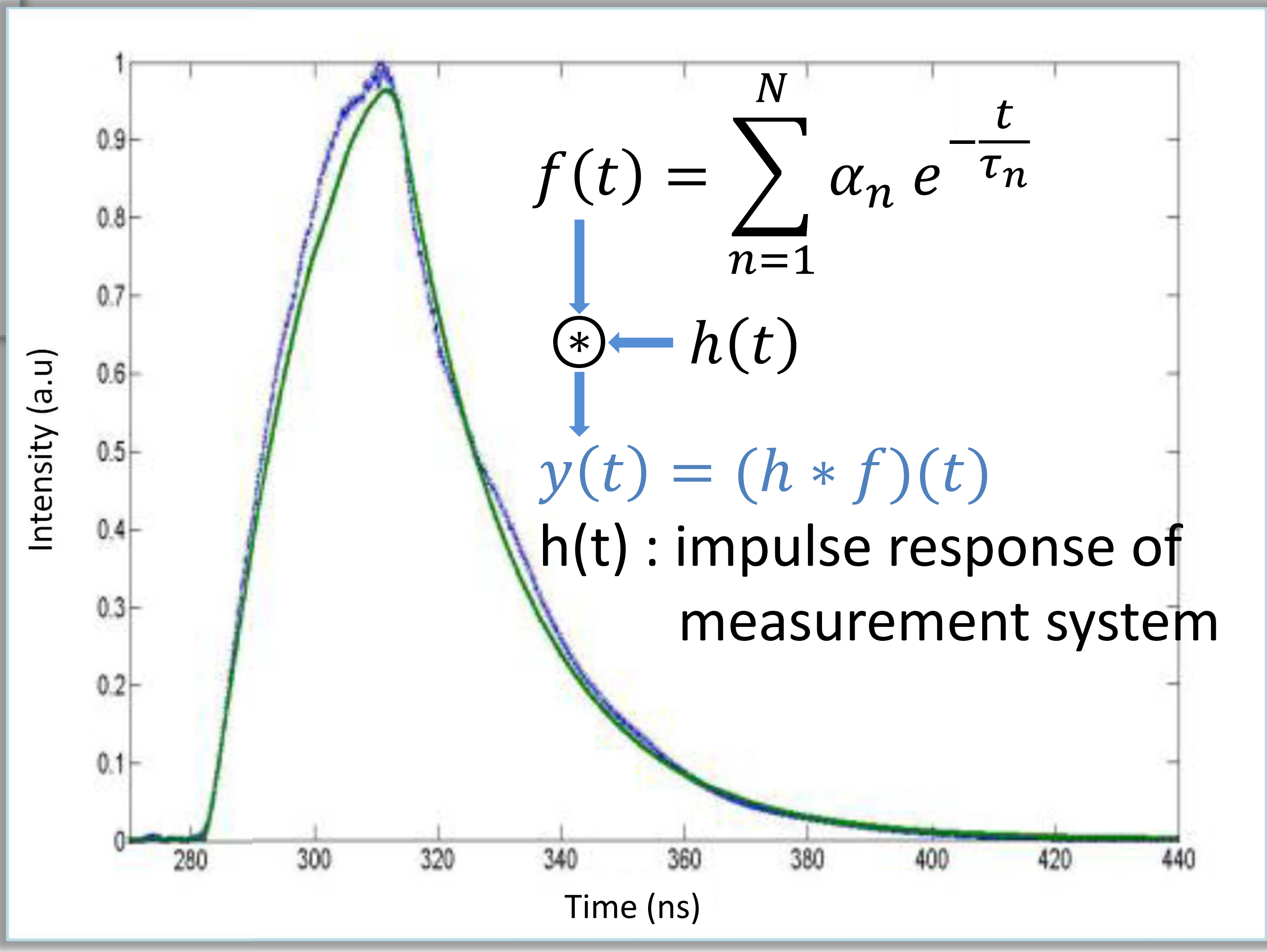


TIME RESOLVED LASER SPECTROSCOPY

- Time evolution model



$$\int_\lambda$$



$$f(t) = \sum_{n=1}^{N} \alpha_n \, e^{-\frac{t}{\tau_n}}$$

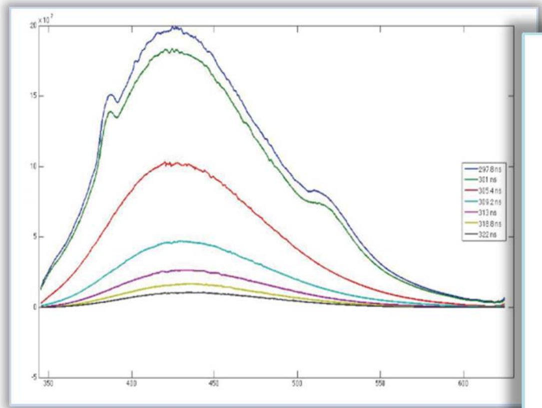
$$\circledast \leftarrow h(t)$$

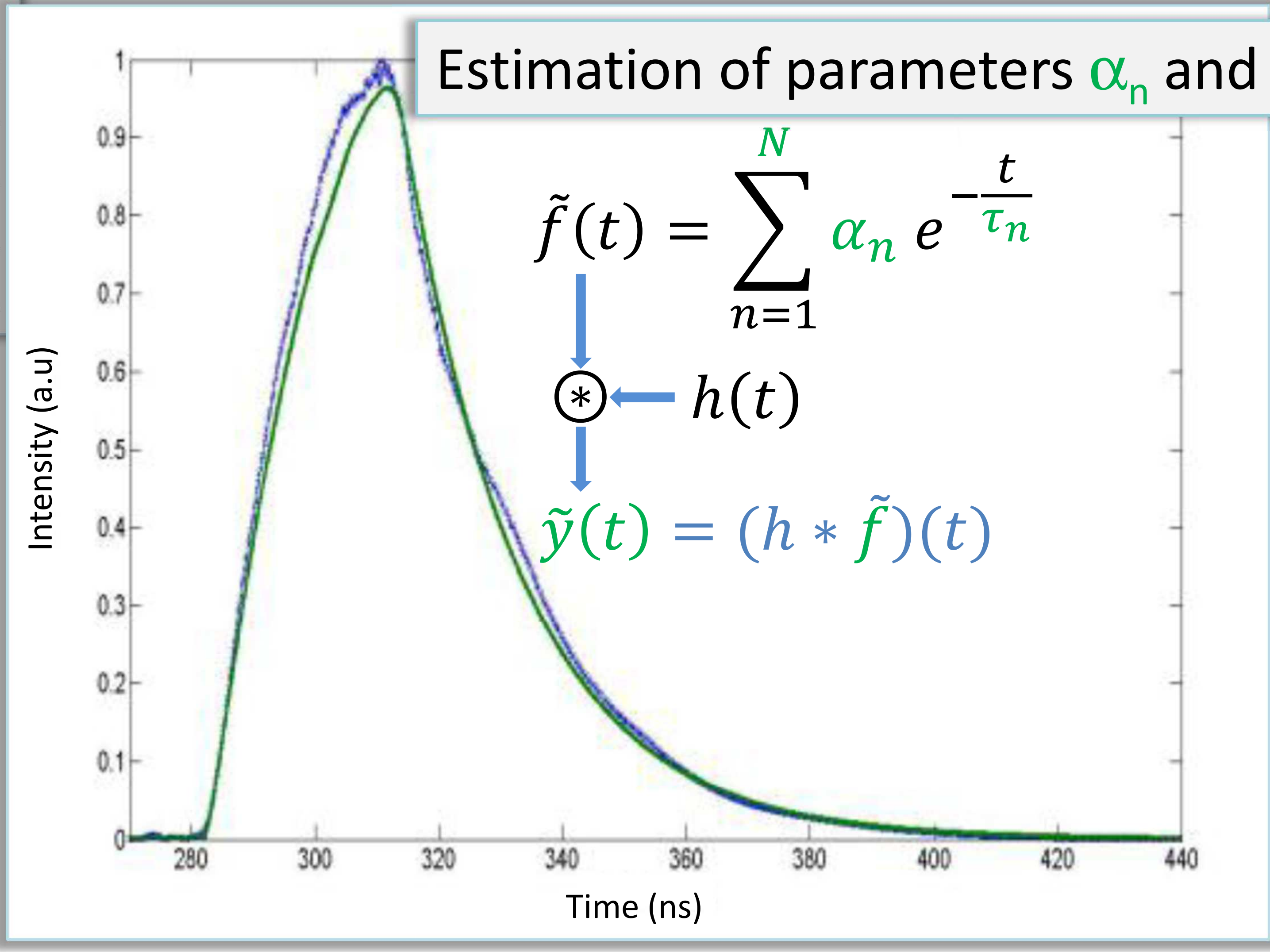
$$y(t) = (h * f)(t)$$

h(t) : impulse response of measurement system

TIME RESOLVED LASER SPECTROSCOPY

- Time deconvolution





Estimation of parameters α_n and τ_n

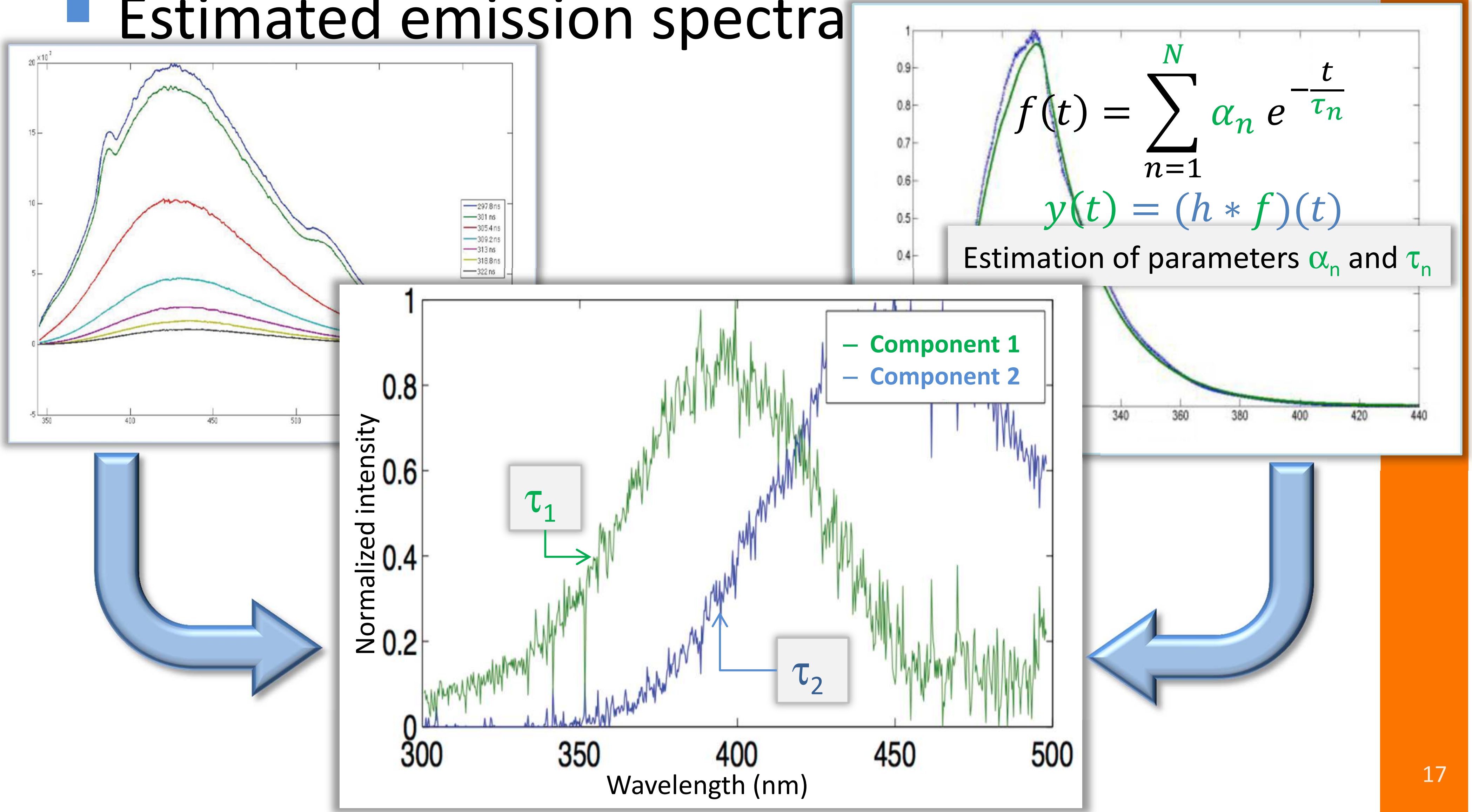
$$\tilde{f}(t) = \sum_{n=1}^{N} \alpha_n \, e^{-\frac{t}{\tau_n}}$$

$$\circledast \leftarrow h(t)$$

$$\tilde{y}(t) = (h * \tilde{f})(t)$$

TIME RESOLVED LASER SPECTROSCOPY

- Estimated emission spectra



TIME RESOLVED LASER SPECTROSCOPY

- Picosecond tunable laser

- Picosecond laser
  - Wavelength: 1064 nm
  - Pulse duration (half-width): 30 ps
  - Energy: 50 mJ
  - Repetition rate: 20 Hz

TIME RESOLVED LASER SPECTROSCOPY

- Picosecond tunable laser

- Picosecond laser
  - Wavelength: 1064 nm
  - Pulse duration (half-width): 30 ps
- Harmonic generator
  - Wavelengths: 1064 nm, 532 nm, 355 nm and 266 nm
- Optical Parametric Oscillator (OPO)
  - Wavelength ranges: 210 nm - 340 nm, 379 nm - 419 nm, 420 nm - 680 nm, and 740 nm - 2300 nm

APPLICATIONS

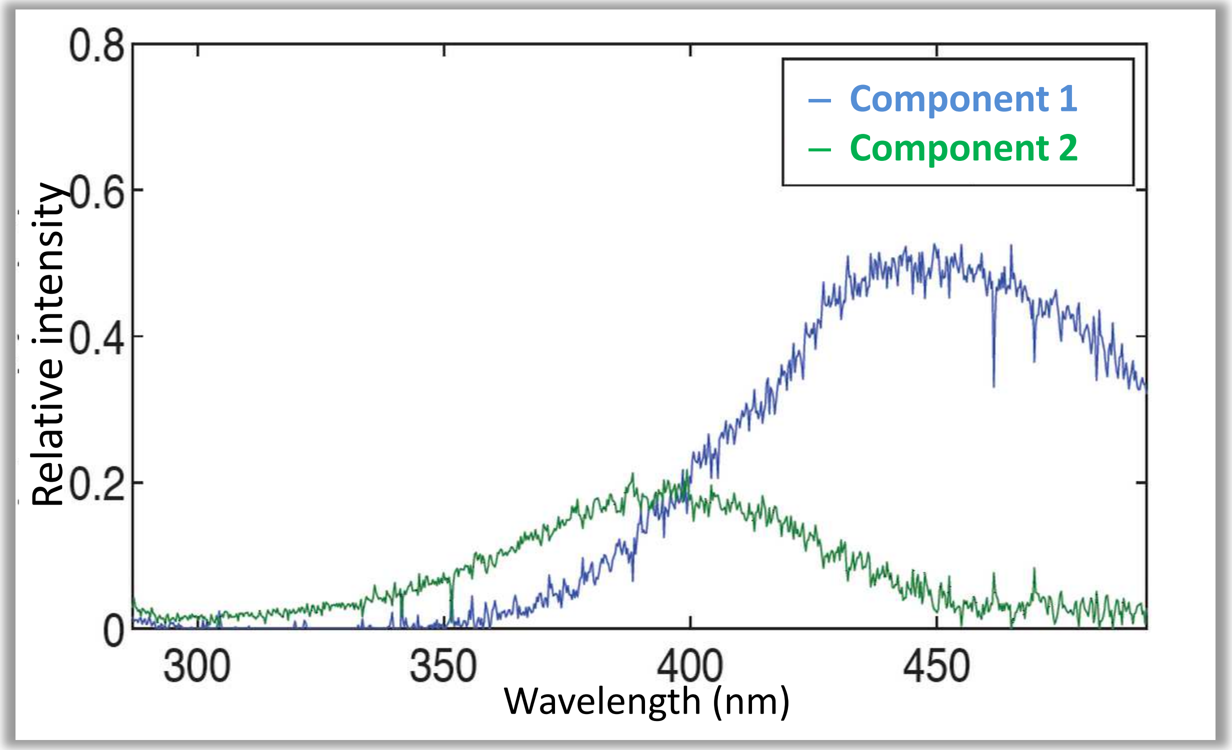
- Liquid samples
  - Standard molecules
    - Estimated emission spectra and lifetimes obtained by TRLF
    - Good agreement with the results from the literature
    - Validation of the measurement system
  - Natural Organic Matter (NOM)
    - Comparison with spetral contributions obtained by spectrofluorimetry and trilinear decomposition
    - Estimated lifetime of fluorescent components

APPLICATIONS

- Liquid samples
  - NOM + PAH
    - Polycyclic aromatic hydrocarbons
    - Controlled mixtures of NOM and PAH
    - Same spectral contributions obtained previously
    - Detection threshold lower than those obtained by chromatography for certain PAH
- Solid samples
  - OLED
    - Spectral contributions
    - Fluorescence and phosphorescence lifetimes

APPLICATIONS

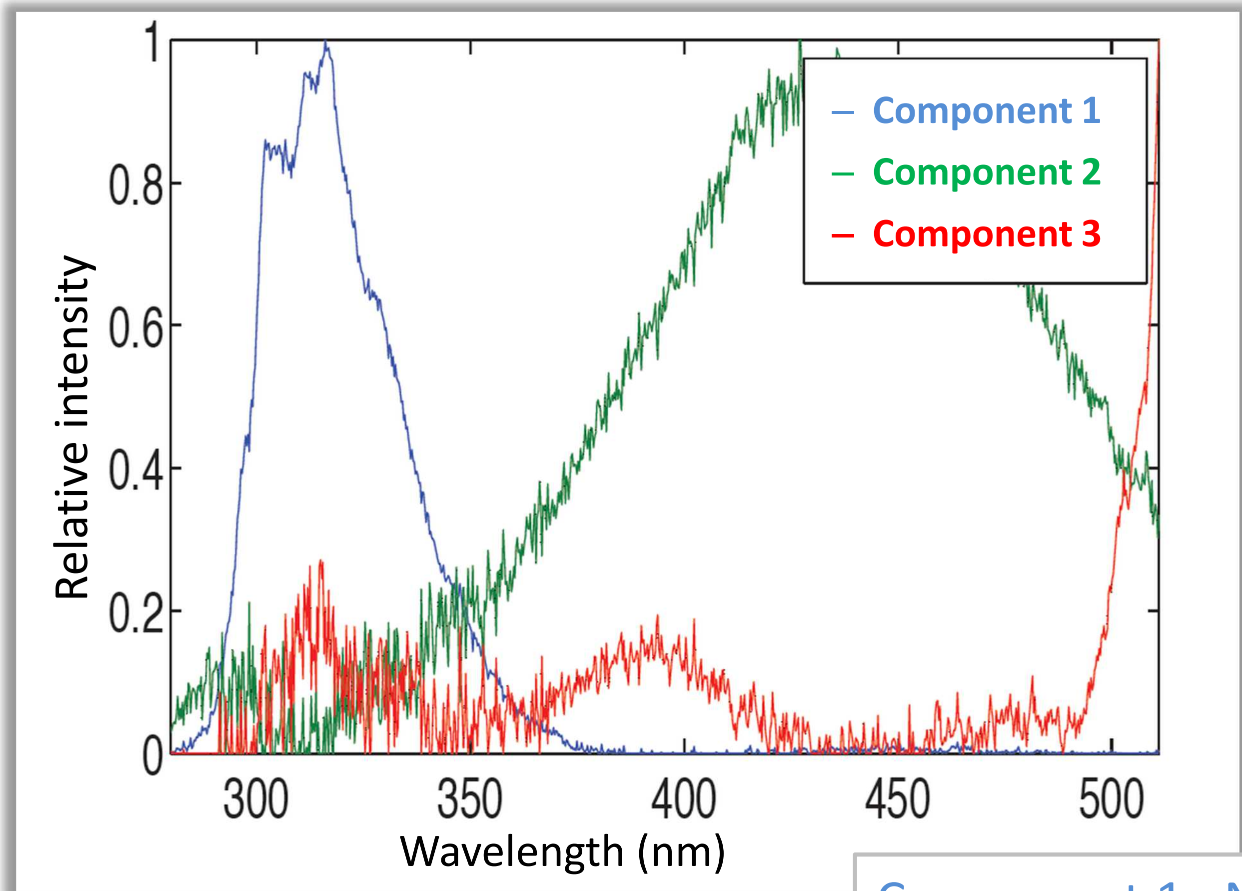
- Natural Organic Matter (NOM)



Component 1 : fulvic acid (τ_1 = 1,1 ns)
Component 2 : humic acid (τ_2 = 7,0 ns)

APPLICATIONS

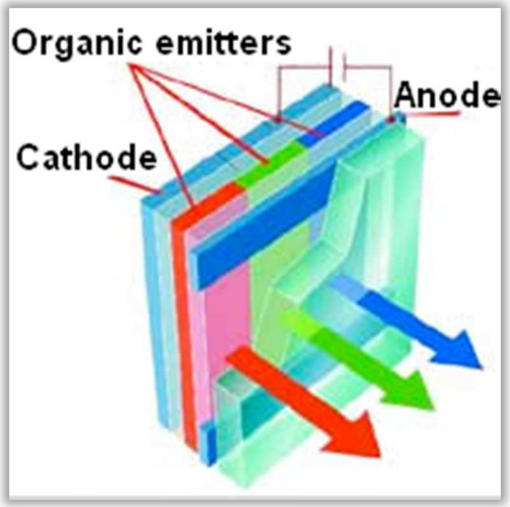
- Natural Organic Matter and PAH

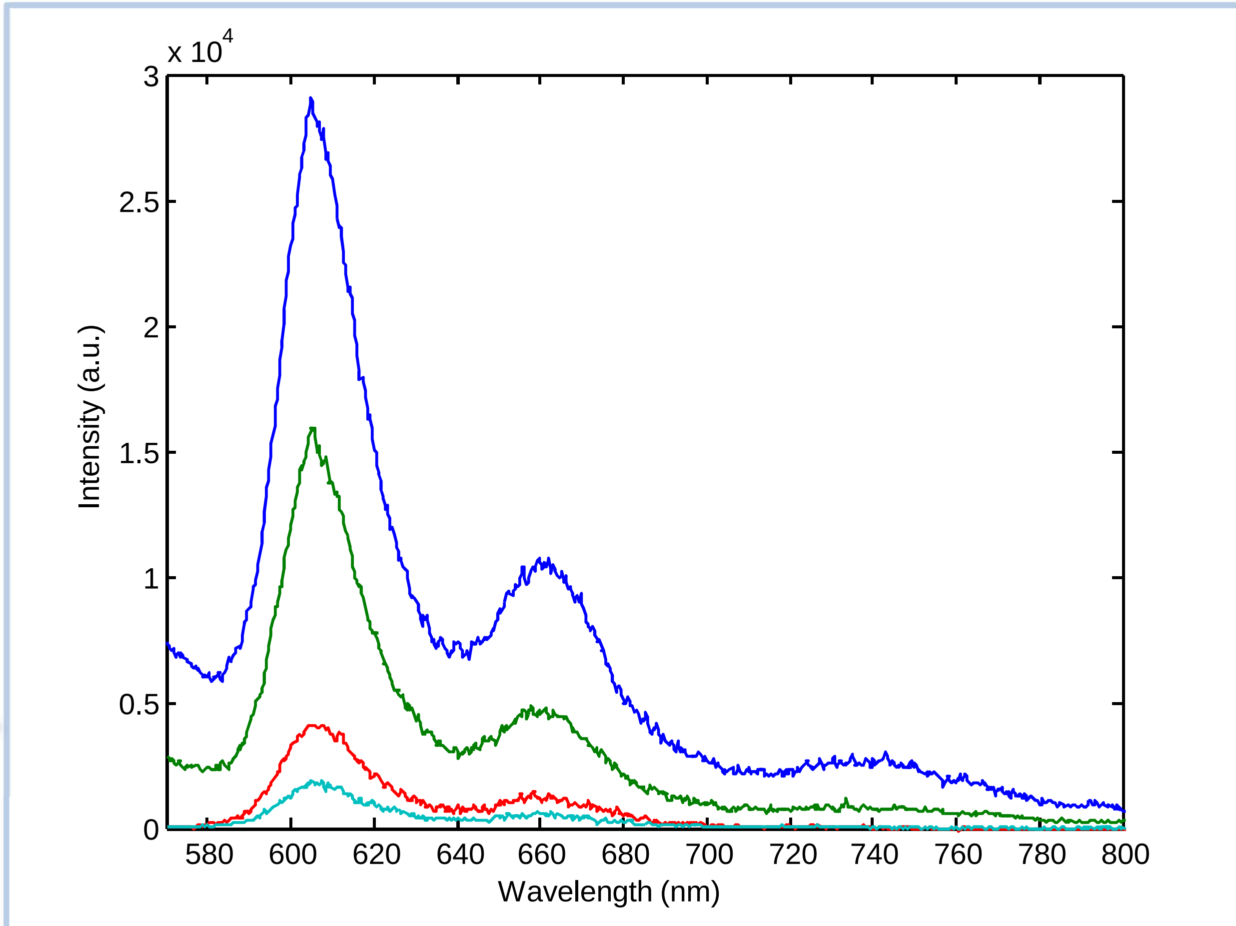


Component 1 : Naphtalen (τ_1 = 28,5 ns)
Component 2 : NOM (τ_2 = 6,3 ns)
Component 3 : Rayleigh scattering (τ_3 = 0,8 ns)

APPLICATIONS

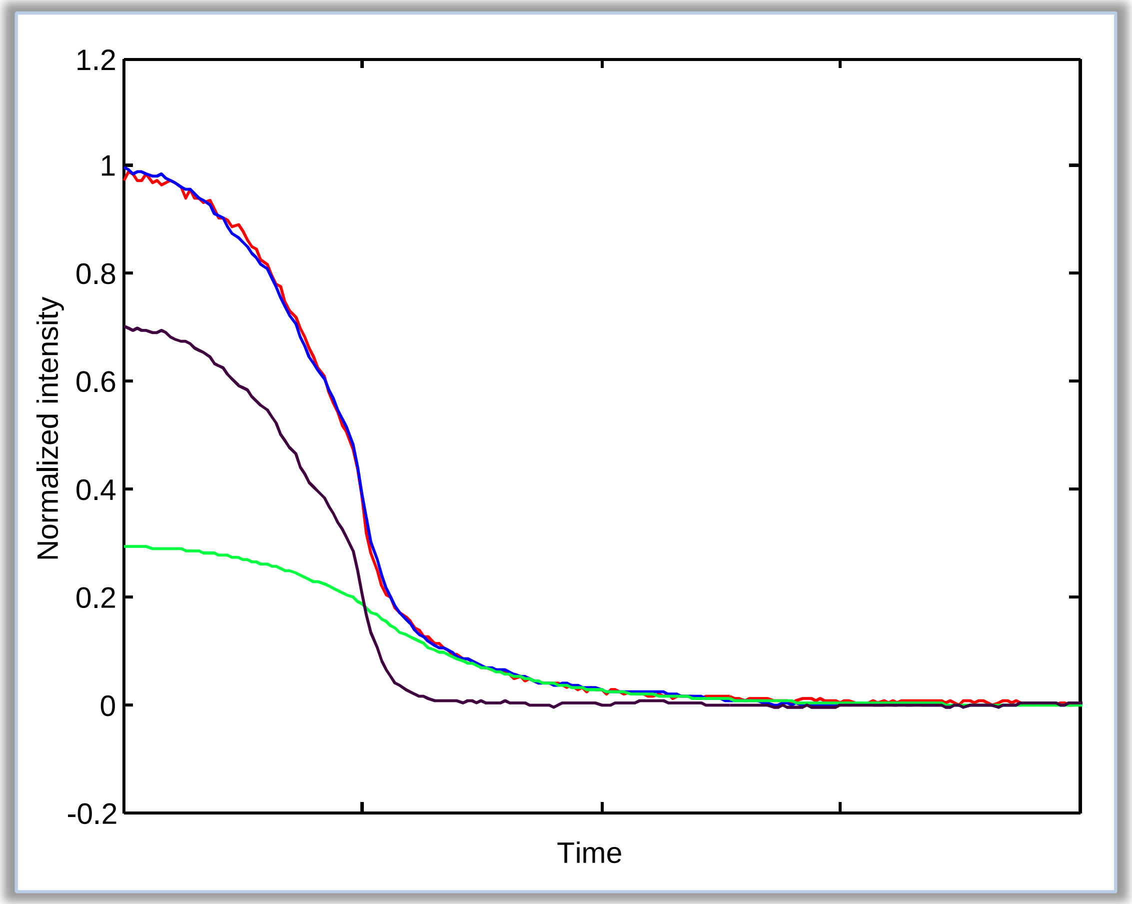
- OLED
  - Time evolution of emission spectra





APPLICATIONS

- OLED
  - Time evolutions



Measured fluorescence
Modelised fluorescence
Contribution 1 (τ_1)
Contribution 2 ($\tau_2 > \tau_1$)

FLUOROPOLE

- Partners

DEI/SECRE/LRE (IRSN Cadarache)

LRSAE (UNSA)

LCE-LCP (Aix-Marseille Université)

Envolure – INRA Montpellier

NUPEGEL (Universidade de São Paulo)