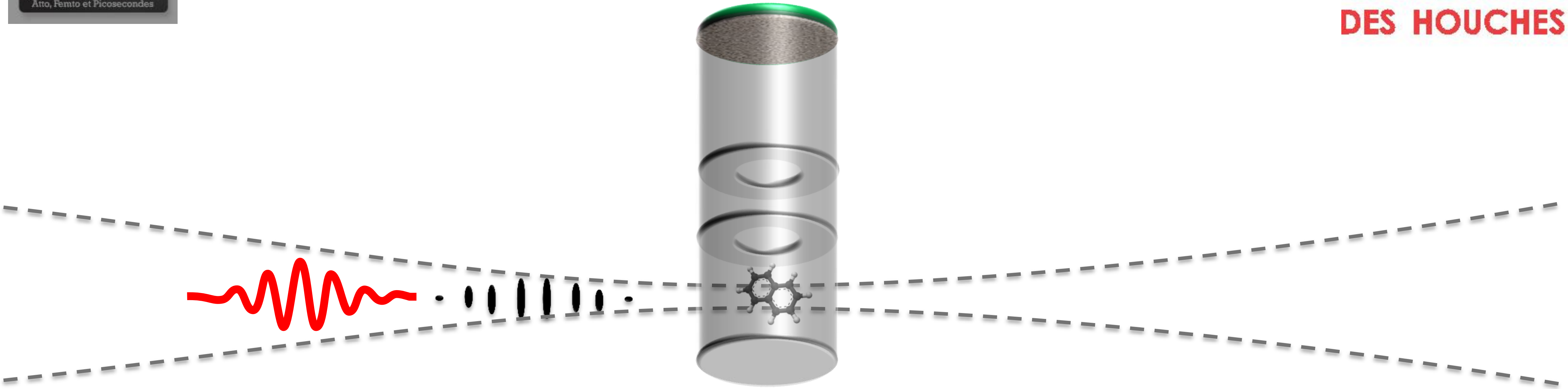
GDR EMIE

"Experimental toolbox to follow the molecular dynamics"



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Research group : Multiscale Dynamics of Complex Molecules

Outline

- Introduction
  - Molecular timescales
- Toolbox description
  - Ultrashort laser pulses measurements (SHG and SHG-Scan)
  - Time Resolved Velocity Map Imaging (TR-VMI)
- Signal acquisition
  - General framework for time-resolved acquisition
- Chose your toolbox, start to practice

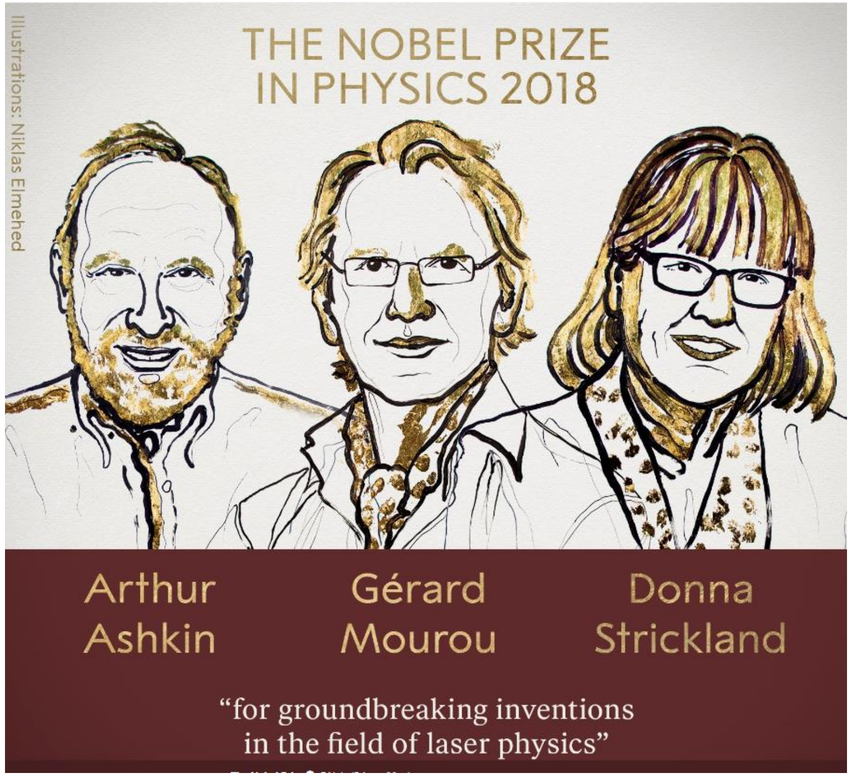
GNU Octave
https://www.gnu.org/software/octave/

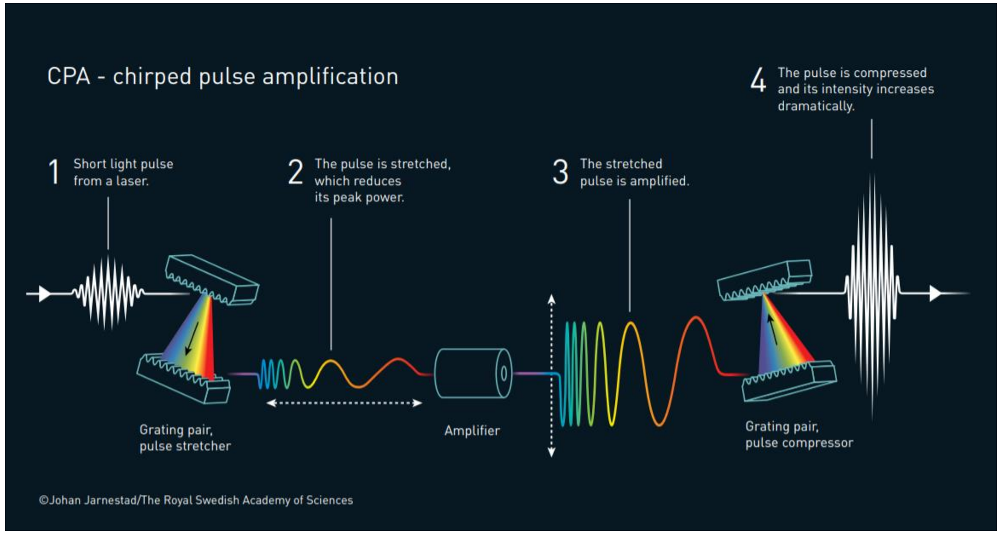
https://fr.mathworks.com/products/matlab.html

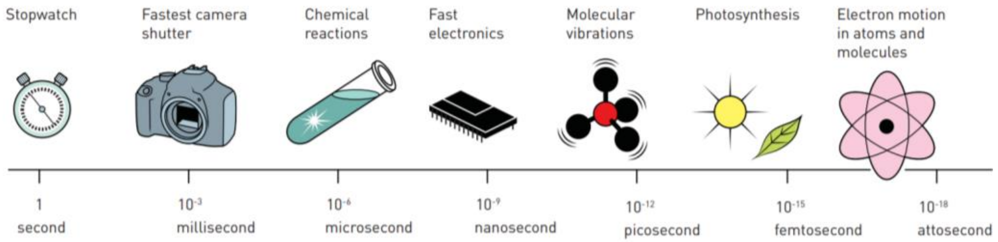
Outline

Introduction

2018 Nobel prize for ultrafast technology







https://www.nobelprize.org/prizes/physics/2018/summary/

The ultrafast timescale

Def: The term ultrafast is employed for processes that takes place bellow the nanosecond timescale

10^{-3}s	10^{-6}s	10^{-9}s	10^{-12}s	10^{-15}s	10^{-18}s	10^{-21}s	
milli	micro	nano	pico	femto	atto	zepto	second

Rotations

The rotational constant of a small diatomic molecule is about 10 ps

Vibration

The vibrational constant of a small diatomic molecule is about 10 fs

Electron

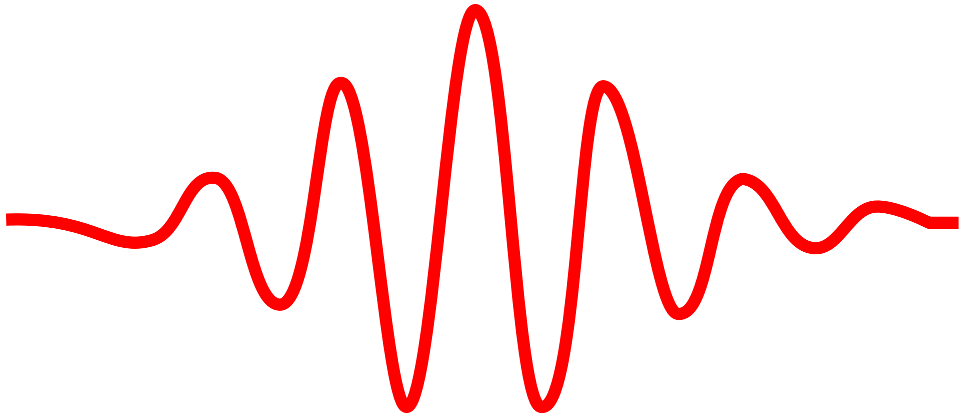
In the Bohr model, the electron orbit around the hydrogen atom in about 150 as

Ultrafast science and molecular physics

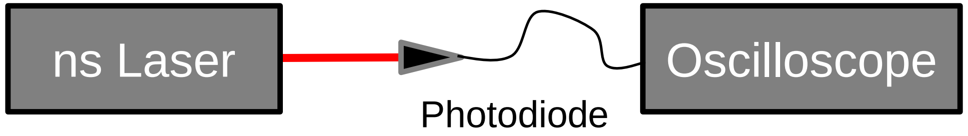
Ultrafast science allows to time-resolve the molecular dynamics

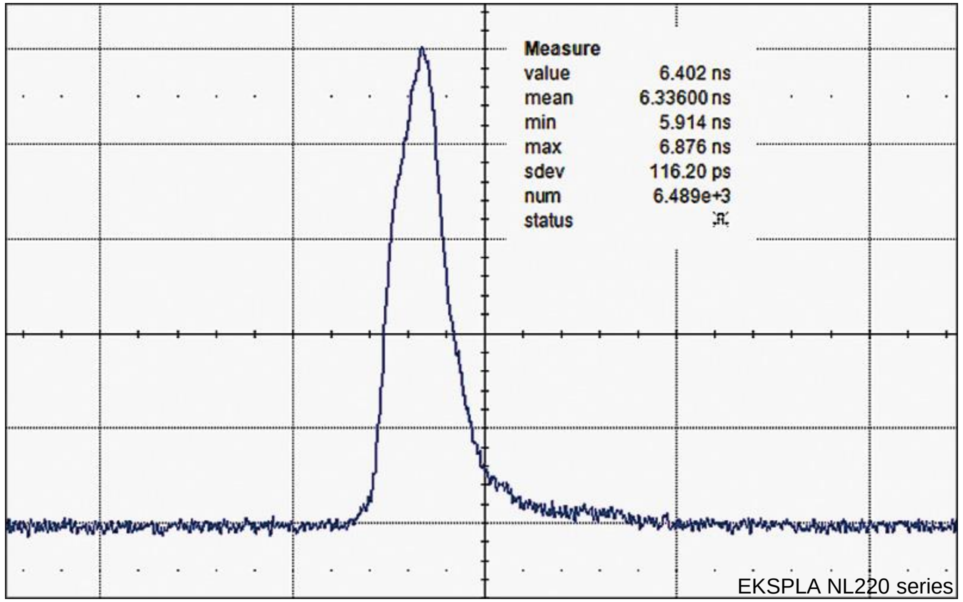
Attoscience allows to time resolve the electronic dynamics inside a molecule

Toolbox – SHG & Pulse measurement



Toolbox – Pulse Measurement – Introduction





ns/ps laser

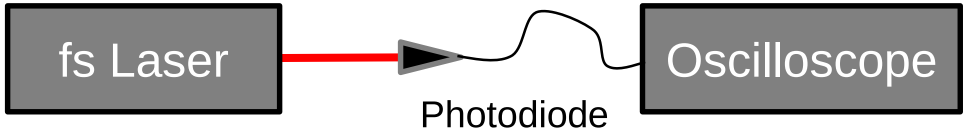
The temporal profile is measured by a photodiode and imaged on an oscilloscope

Photodiode and oscilloscope limit

The limit of this technique is

~10 GHz (i.e. 100 ps)

Since electrons propagates slower that photons, no electronic solution is possible in the temporal domain



$$S(t) = R(t) \times \int_{-\infty}^{\infty} I(t)dt$$

Pulse temporal profile

Electronic shortest response

Signal on the oscilloscope

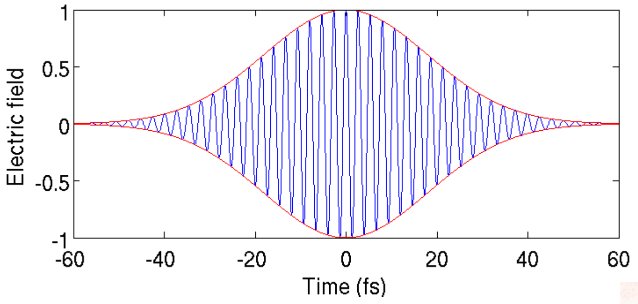
No direct measurement possible

Always the same signal measured on the oscilloscope with a magnitude that corresponds to the pulse energy

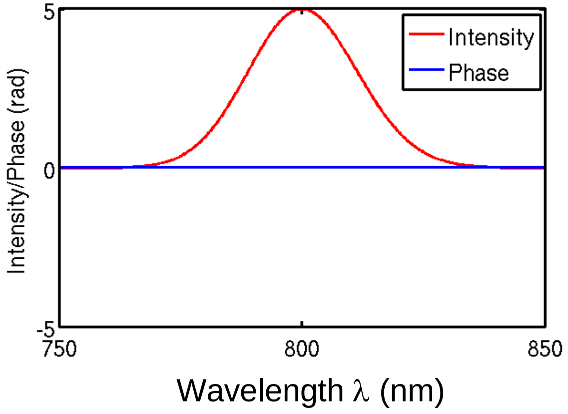
Toolbox – Pulse Measurement – Spectral approach

Temporal amplitude and phase **OR** Spectral amplitude and phase

$$\tilde{E}(t) = E(t)e^{i\phi(t)}$$



$$\tilde{E}(\omega) = E(\omega)e^{-i\phi(\omega)}$$



!! Representaiton !!

It is always represented the spectral phase :

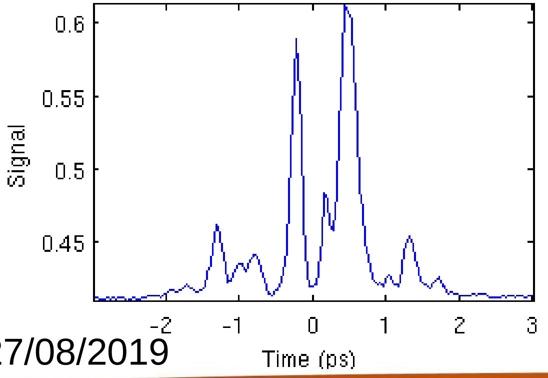
ϕ(ω)=arg(E(ω))

And the spectral intensity

I(ω) = |E(ω)|²

$$\mathcal{TF}: \ \tilde{E}(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \tilde{E}(\omega)e^{i\omega t}d\omega$$

$$\mathcal{TF}^{-1}: \ \tilde{E}(\omega) = \int_{-\infty}^{\infty} \tilde{E}(t)e^{-i\omega t}dt$$



Fourier Transform

Link from the spectral to the temporal domain ℂ ⇆ ℂ

2D information

Toolbox – Pulse Measurement – Phase terms as a Taylor expansion

Fourier Transform : C ⇆ C

The dispersion is encoded into the imaginary part of the temporal / spectral electric field

$$\mathcal{TF}: \ \tilde{E}(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \tilde{E}(\omega) e^{i\omega t} d\omega$$

$$\tilde{E}(\omega) = E(\omega) e^{-i\phi(\omega)}$$

Lets consider a smooth spectral phase (i.e. can be described by a Taylor expansion)

$$\phi(\omega) = \phi_0 + \phi_1(\omega - \omega_0) + \phi_2 \frac{(\omega-\omega_0)^2}{2!} + \phi_3 \frac{(\omega-\omega_0)^3}{3!} + \cdots$$

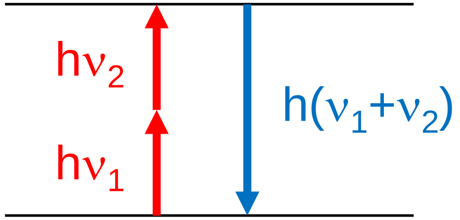
With ϕ_0, ϕ_1, ϕ_2, ϕ_3, … real values that correspond to the dispersion orders respectively in rad, fs, fs^2, fs^3,…

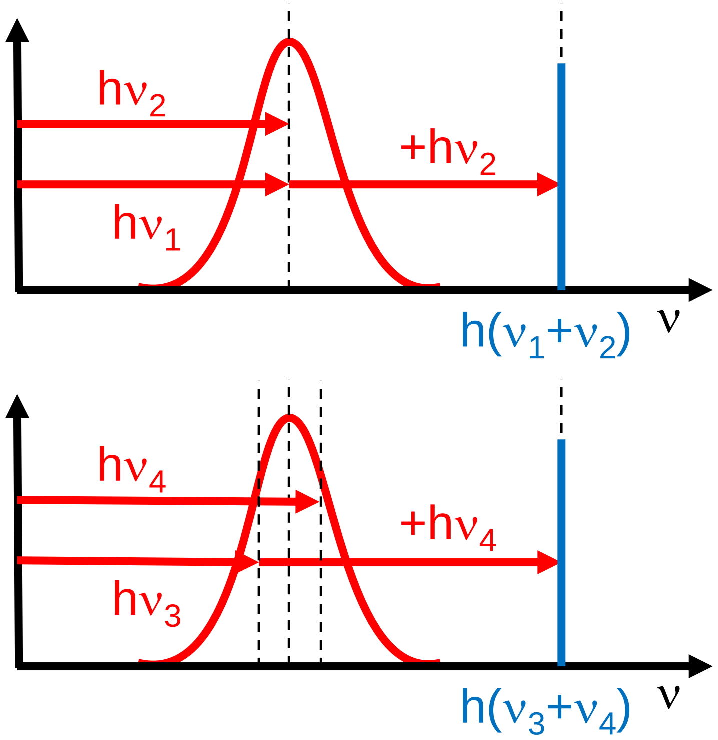
To distinguish the effect of each order of the spectral phase, lets consider the Fourier transform of a pulse with a Gaussian spectral amplitude and a specific order of the spectral phase.

Toolbox – Pulse Measurement – SHG as non-lineal filter

Non-lineal cristal

- When the intensity is high enough (~GW.cm^{-2})
- Non linear crystal sum the frequencies (energy $E=h\nu$)





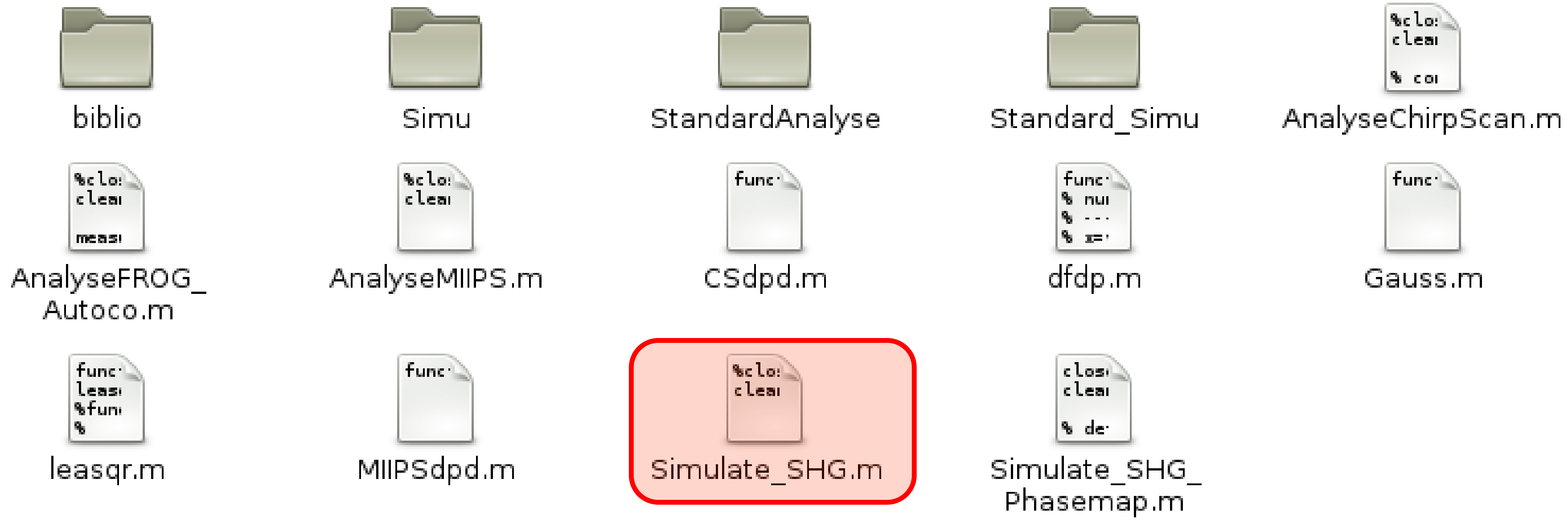
Pathways interferences

- It exists several pathways to generate a given 2nd harmonic
- Each pathway create a wave with a given amplitude and phase
- All the pathways interfere together
- The electric field at 2ω depends on the amplitude an phase of all possible pathways

$$\tilde{E}(2\omega_0) = \int_{-\infty}^{\infty} \tilde{E}\left(\omega_0 - \frac{\delta}{2}\right) \times \tilde{E}\left(\omega_0 + \frac{\delta}{2}\right) d\delta$$

Spectral Auto-convolution

Toolbox – Pulse Measurement – SHG routine



Define the spectral pulse properties of the fundamental pulse (Intensity & phase)

- Representation of the spectral pulse properties of the fundamental
- Representation of the temporal properties of the fundamental and the doubled
- Representation of the spectral pulse properties of the doubled

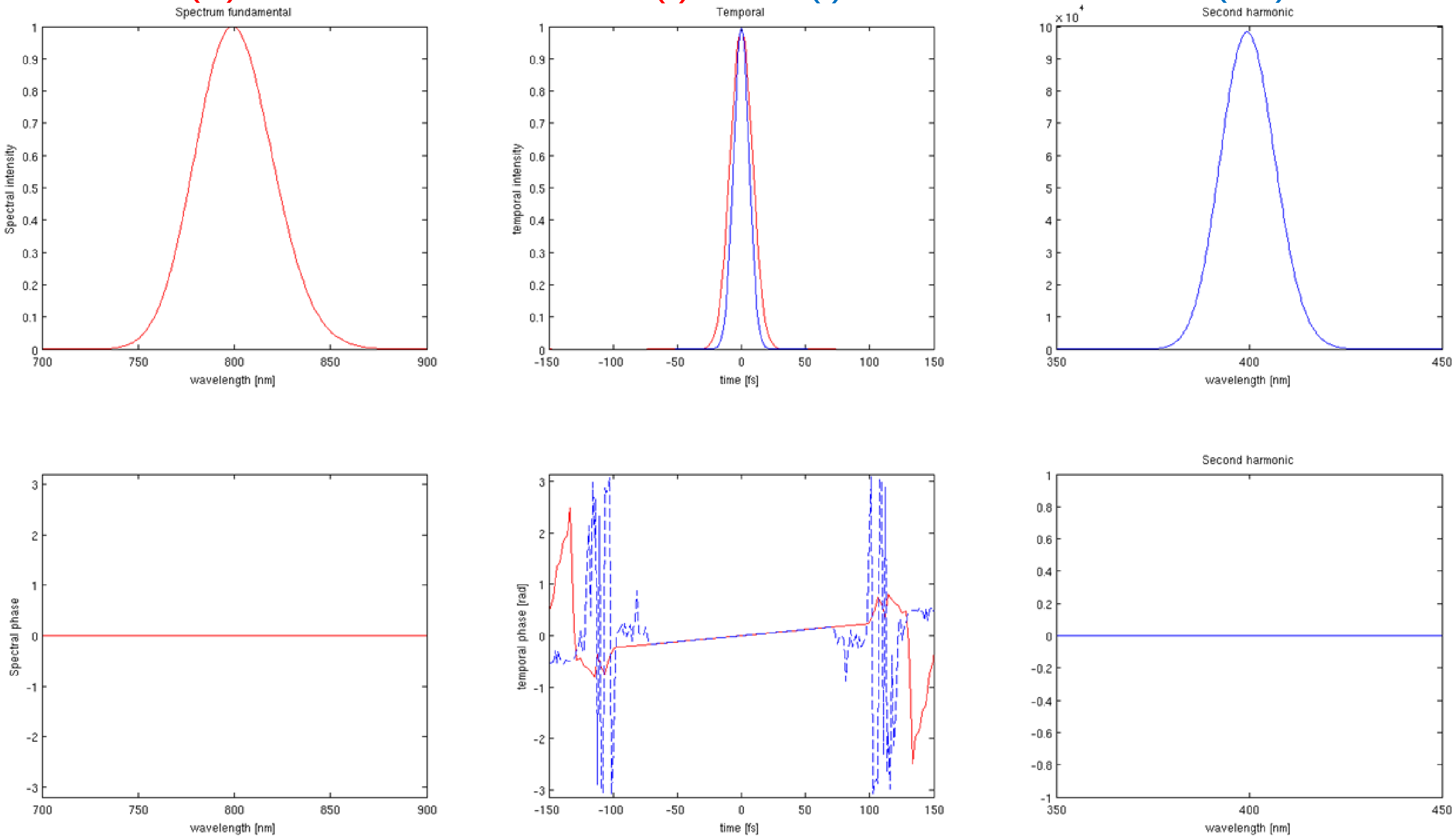
ExpToolbox

Toolbox – Pulse Measurement – SHG routine – Limited Fourier Transform

E(ω) | E(t) and E(t) | E(2ω)

Intensity

phase

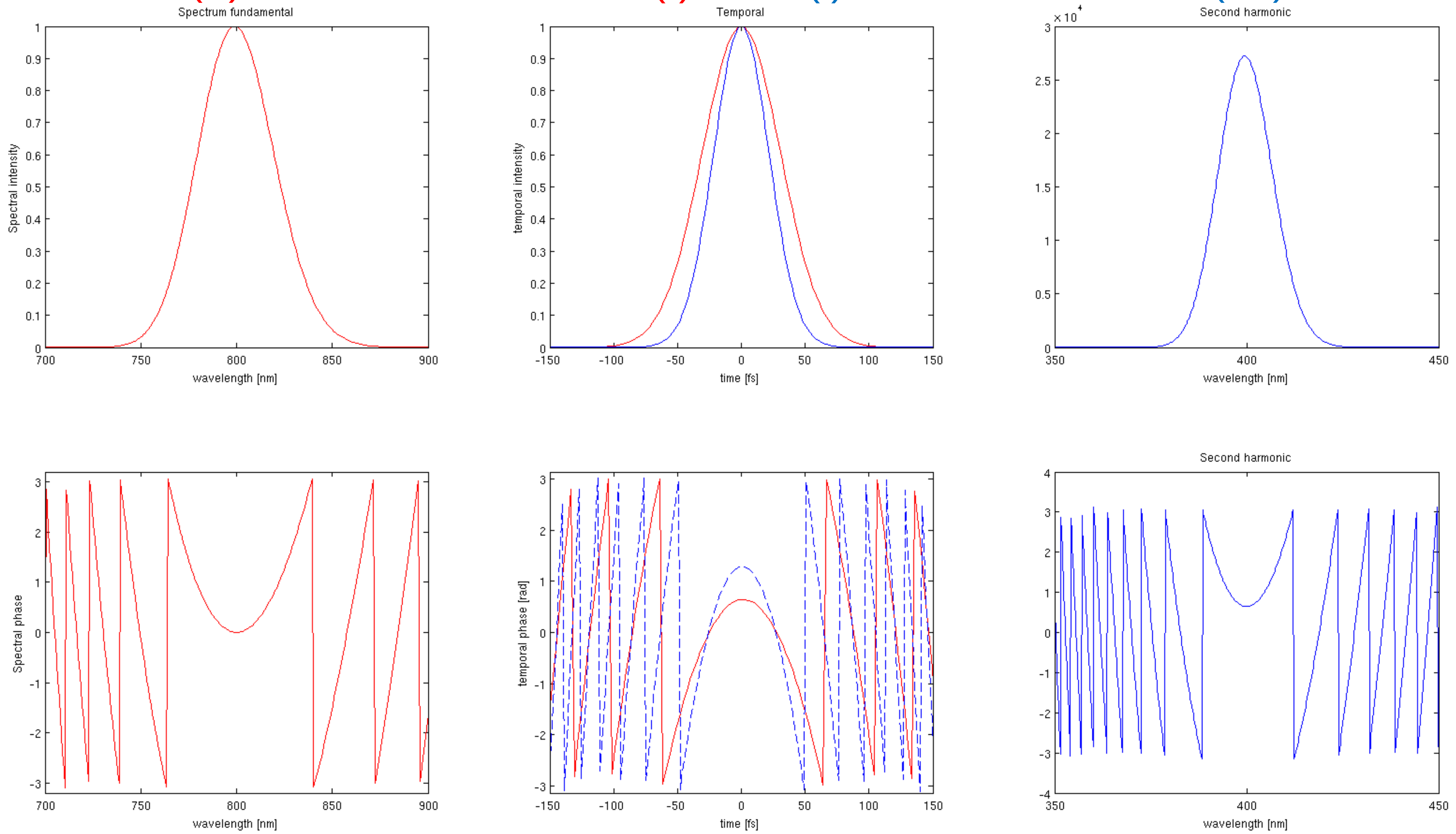


Toolbox – Pulse Measurement – SHG routine – Chirp 500 fs²

E(ω) | E(t) and E(t) | E(2ω)

Intensity

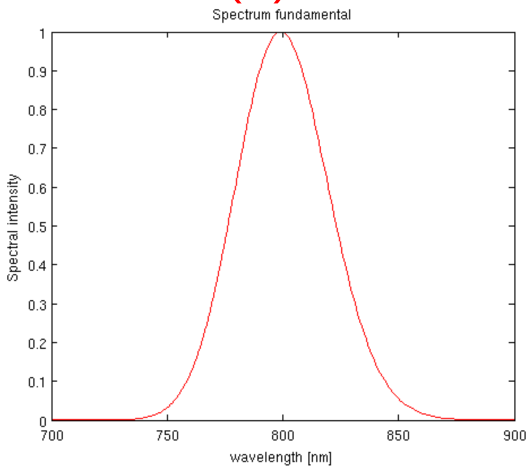
phase

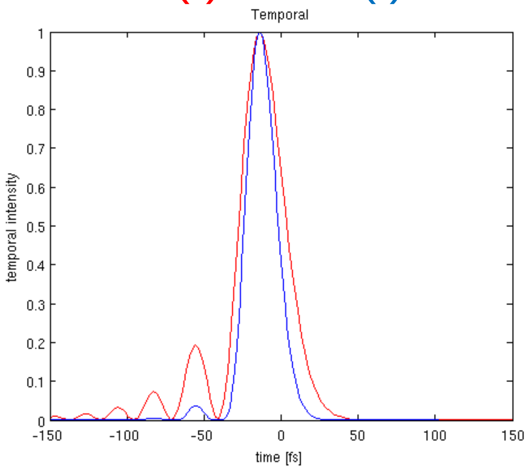


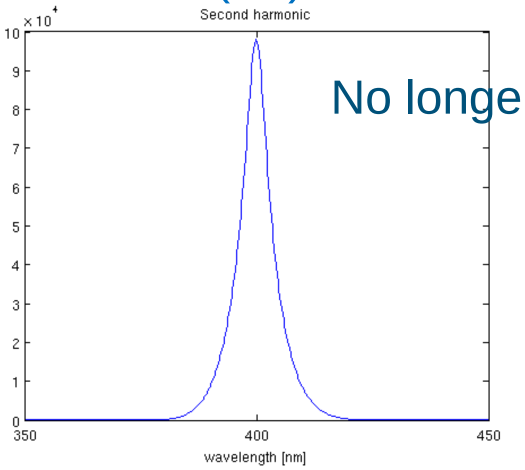
Toolbox – Pulse Measurement – SHG routine – TOD 10 000 fs³

E(ω) | E(t) and E(t) | E(2ω)

Intensity

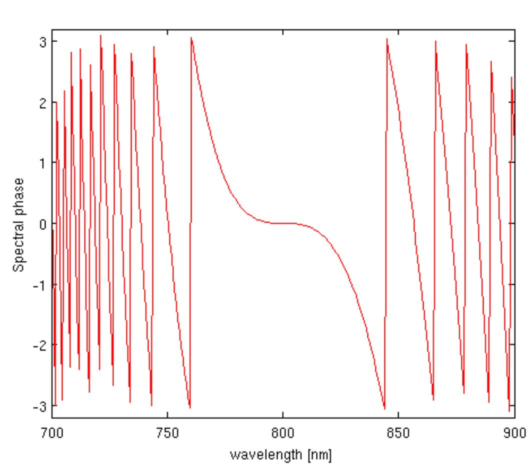


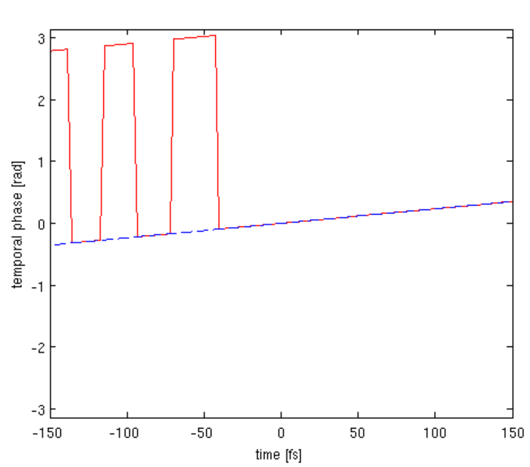


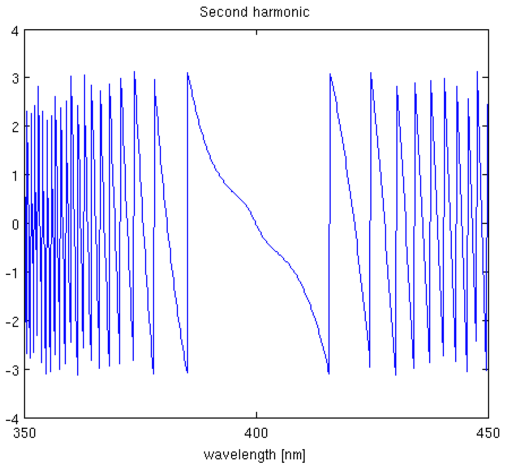


No longer Gaussian

phase





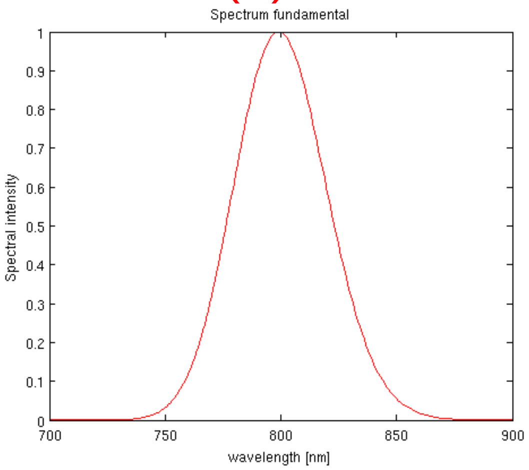


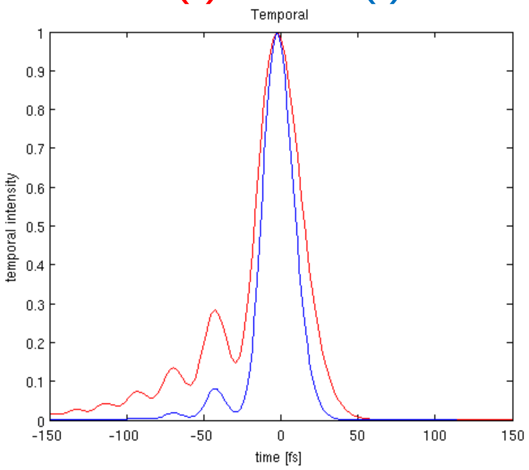
ExpToolbox

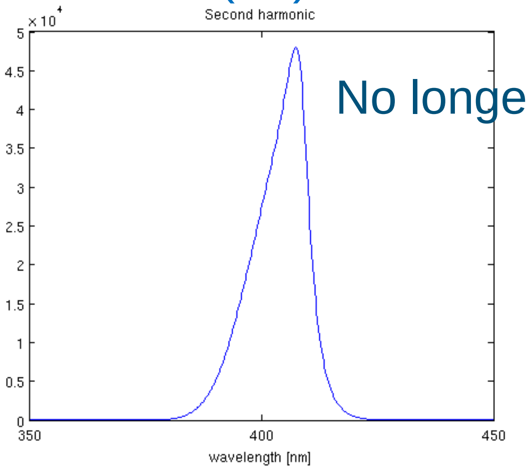
Toolbox – Pulse Measurement – SHG routine – Chirp + TOD

E(ω) | E(t) and E(t) | E(2ω)

Intensity

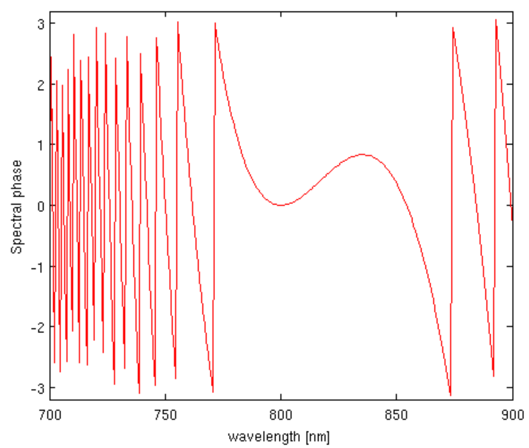


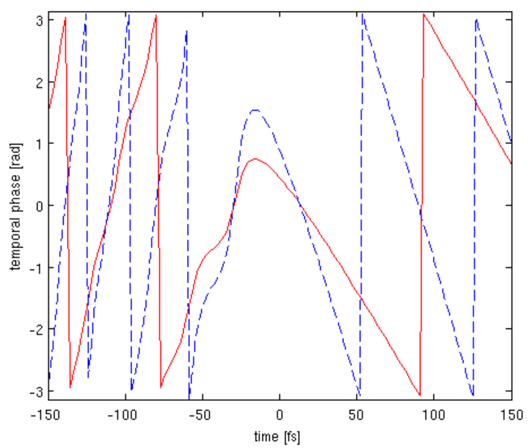


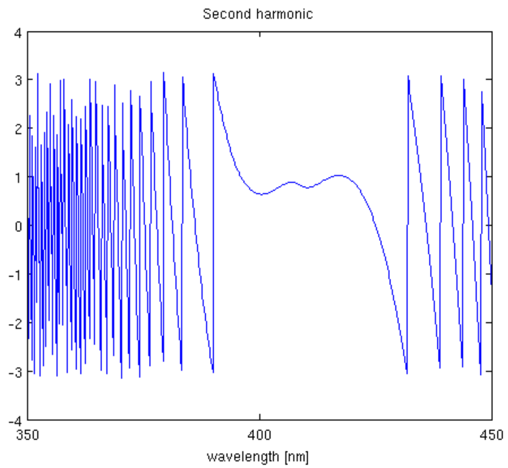


No longer Gaussian

phase







Toolbox – Pulse Measurement – SHG spectrally based methods

Principle:

Chirp-scan	1. Adding a pure chirp	$\phi(\omega)= \phi_{in}(\omega) + \phi_2/2\ (\omega-\omega_0)^2$
d-scan	2. Adding an impure chirp (prism, gratings)	$\phi(\omega)= \phi_{in}(\omega) + \phi_2/2!\ (\omega-\omega_0)^2 + \phi_3/3!\ (\omega-\omega_0)^3+\ldots$
FROG	3. Producing a delayed pulse replica	$\phi_b(\omega)=\phi_a(\omega) + \phi_1/1!\ (\omega-\omega_0)$
MIIPS	4. Introducing a sine function in the spectral phase	$\phi(\omega)=\phi_{in}(\omega) + A \sin(B(\omega-\omega_0)+\phi)$
	…	

Resulting in a 2D information:

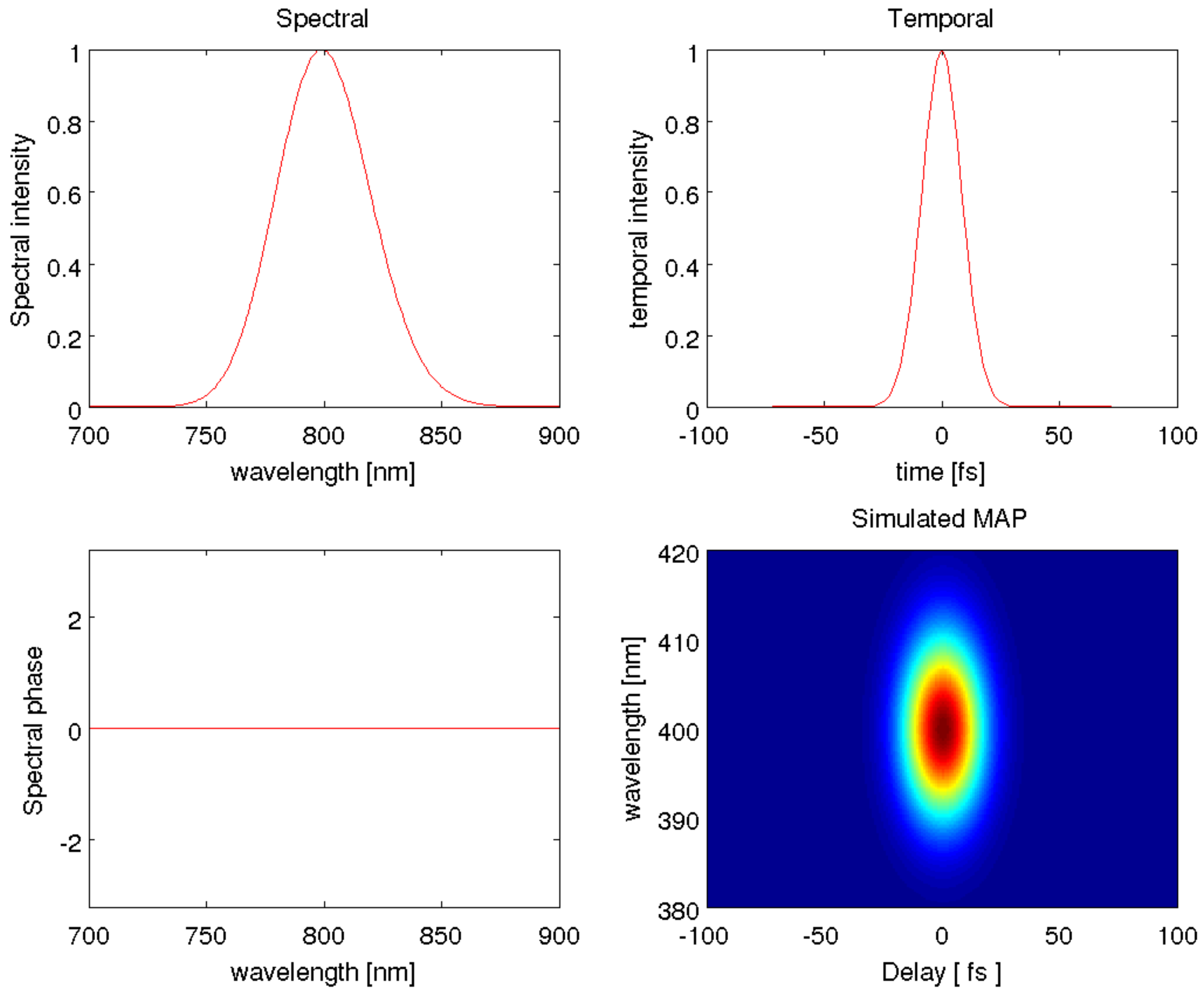
$S(2\omega,\text{parameter})$

-> if the Dimension are independent, possible to reconstruct the 2D caracteristics of the pulse:

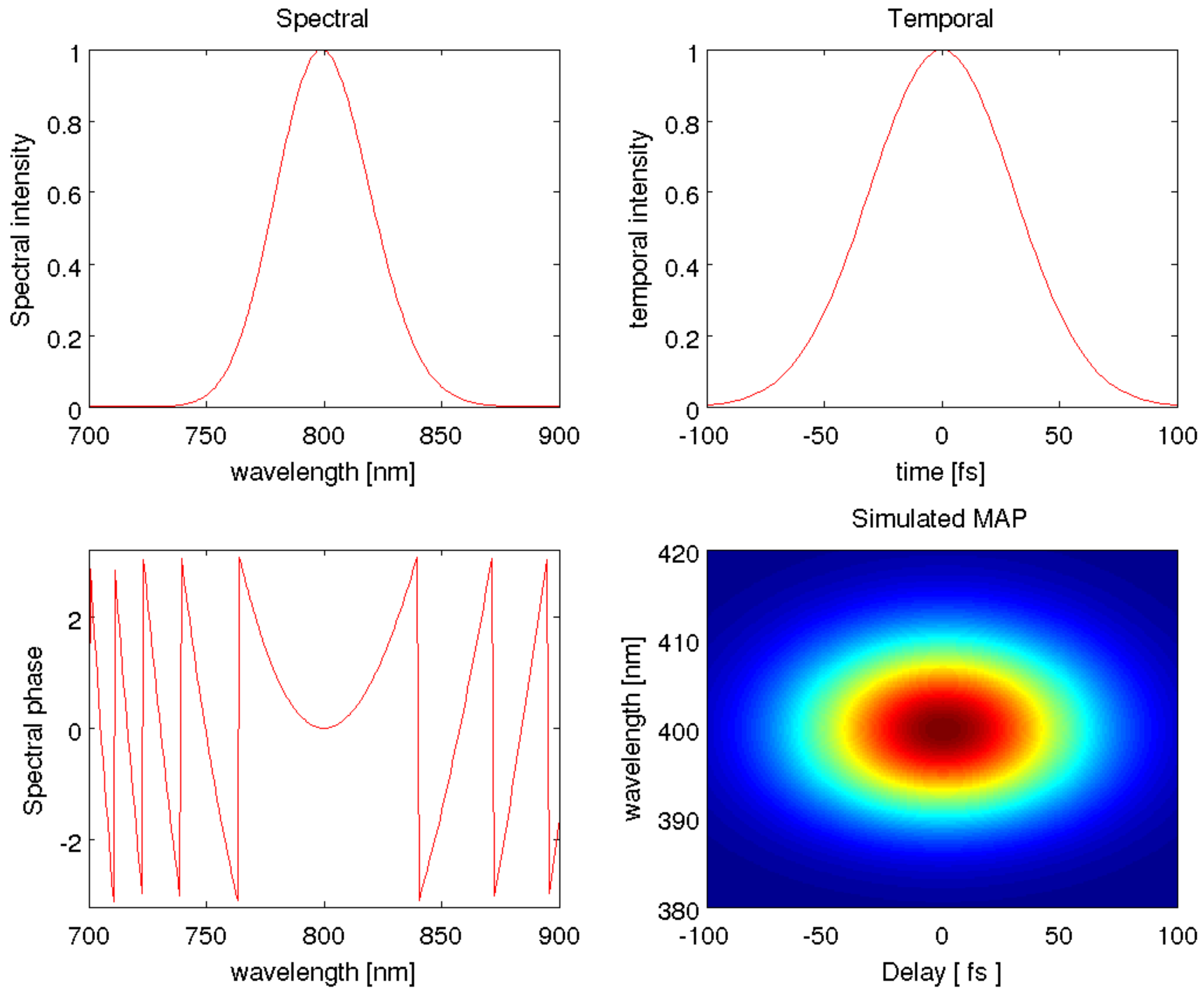
$E(w)=|E_0(w)| \exp(- i\ \phi(\omega))$ => $E(t)$

Presentation on pulse measurement in summer school http://reseau-femto.cnrs.fr/spip.php?article205#

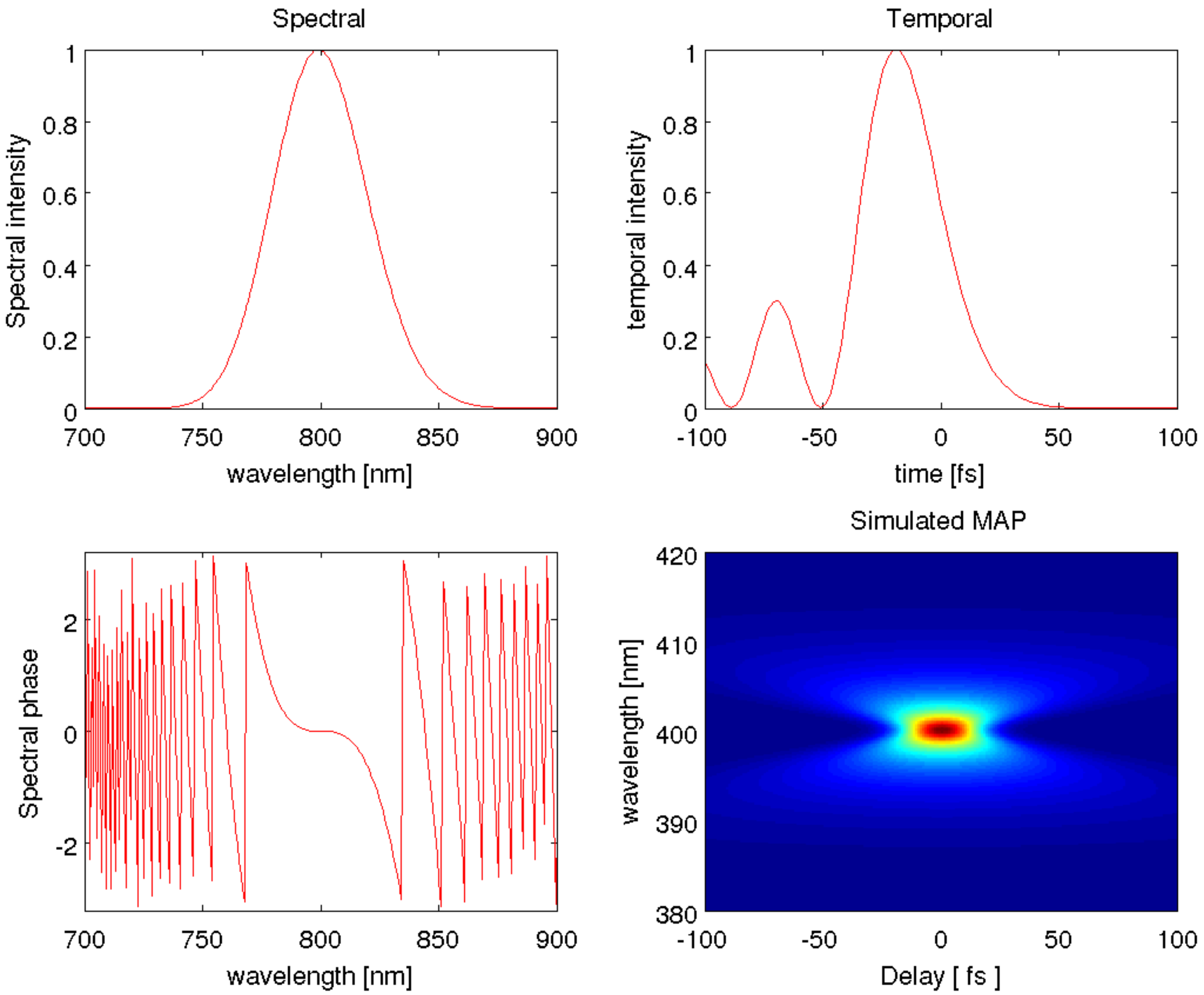
Toolbox – Pulse Measurement – FROG LFT



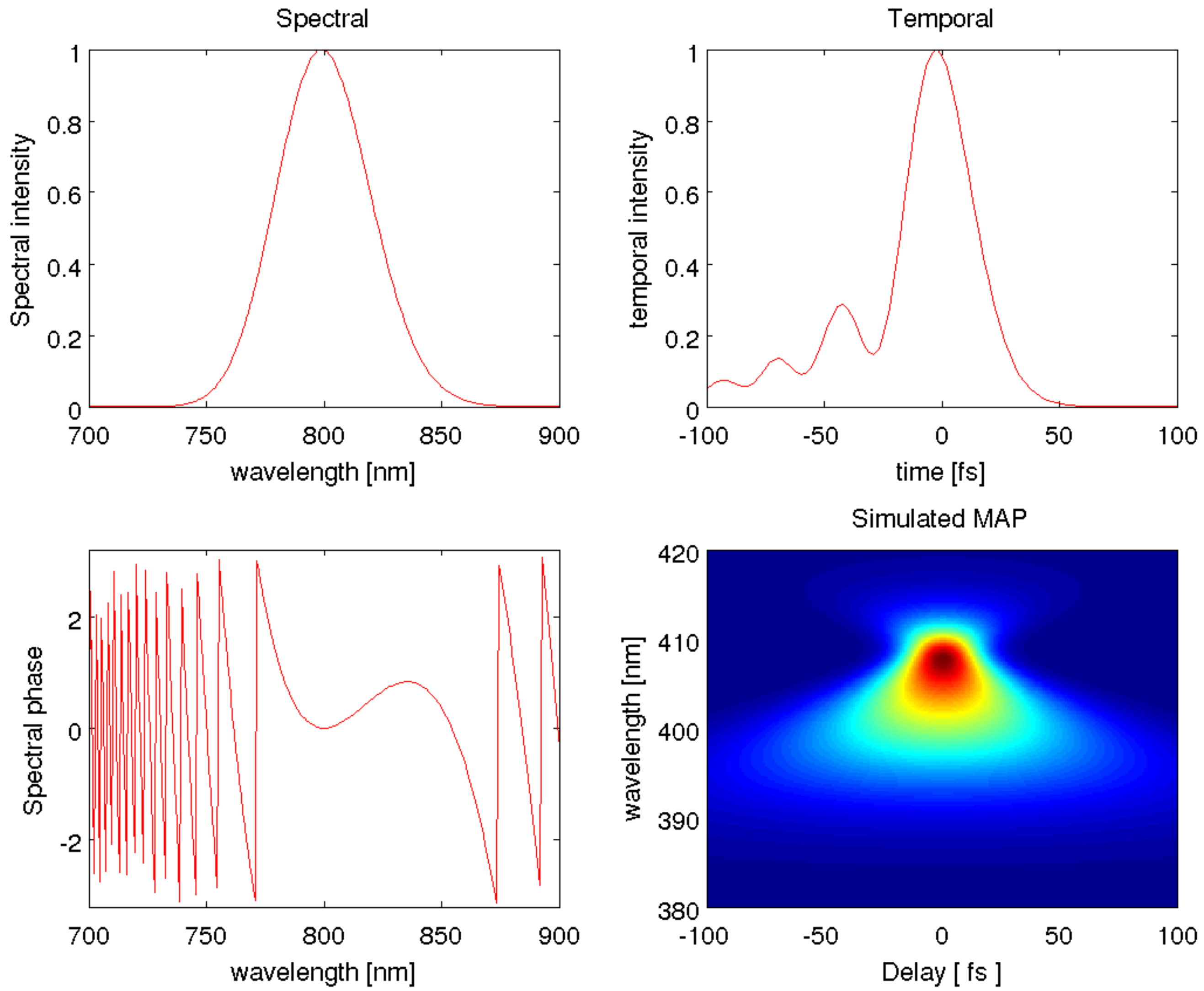
Toolbox – Pulse Measurement – FROG 500 fs²



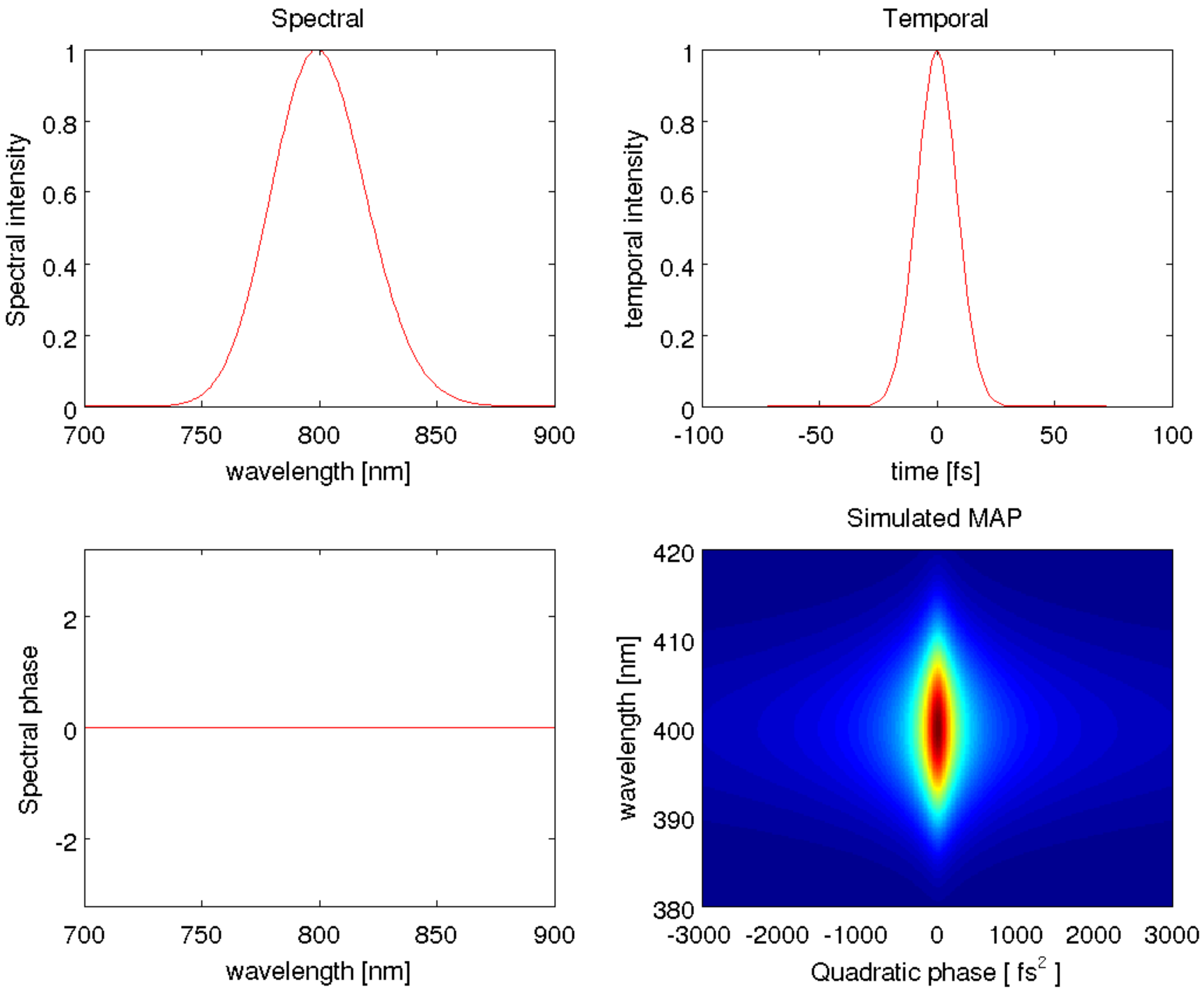
Toolbox – Pulse Measurement – FROG 20 000 fs^3



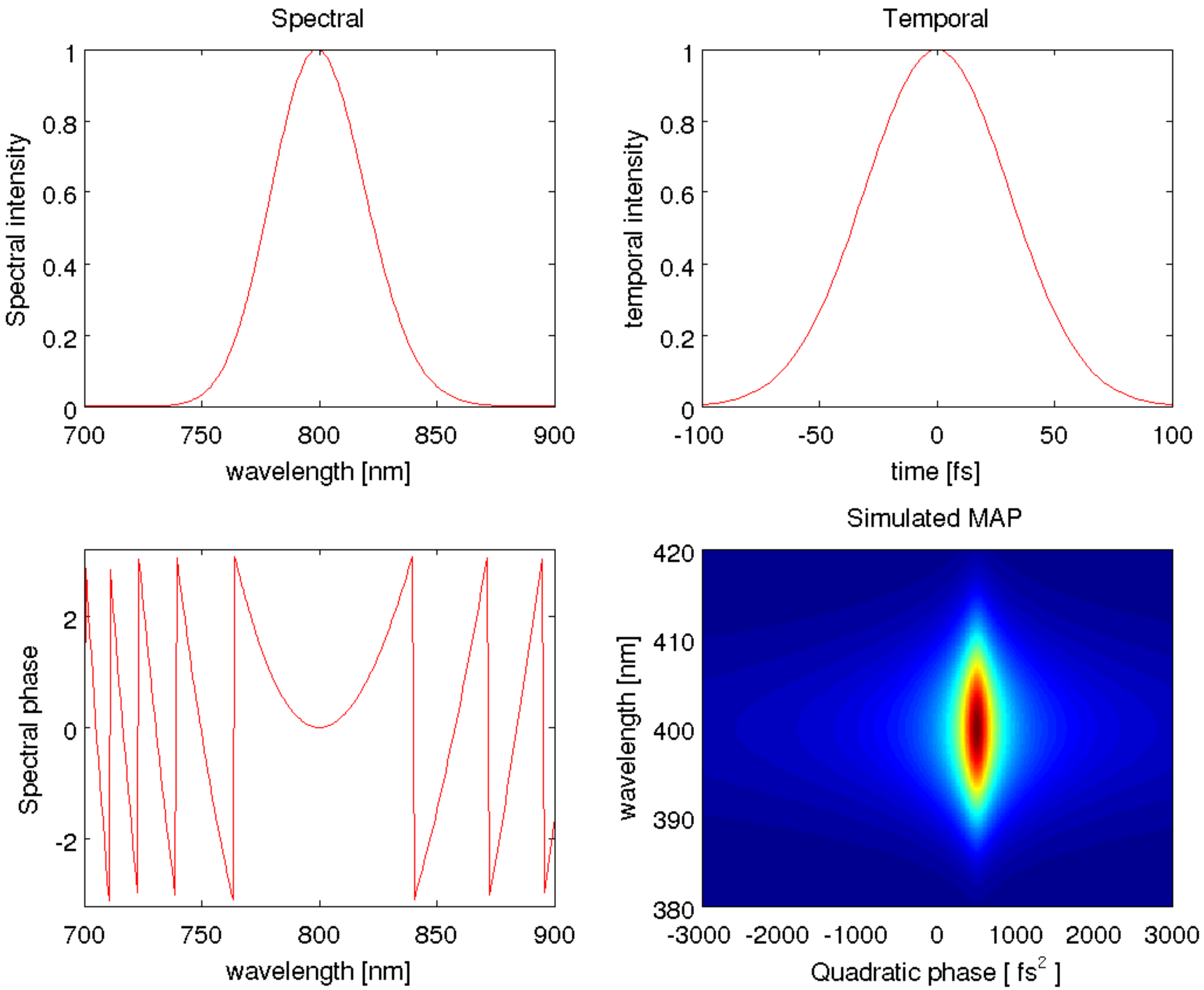
Toolbox – Pulse Measurement – FROG 500 fs² + 20 000 fs³



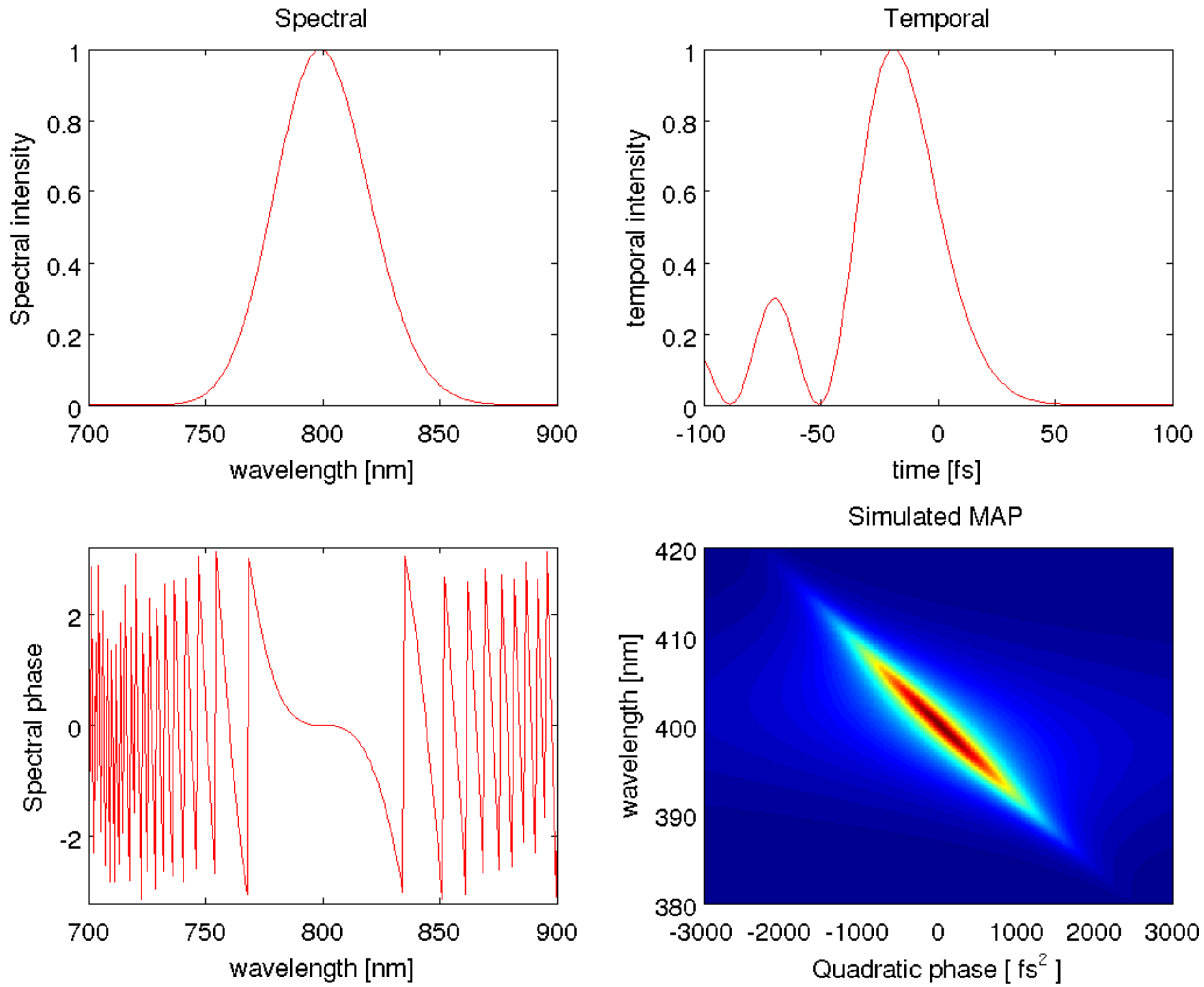
Toolbox – Pulse Measurement – Chirp Scan LFT



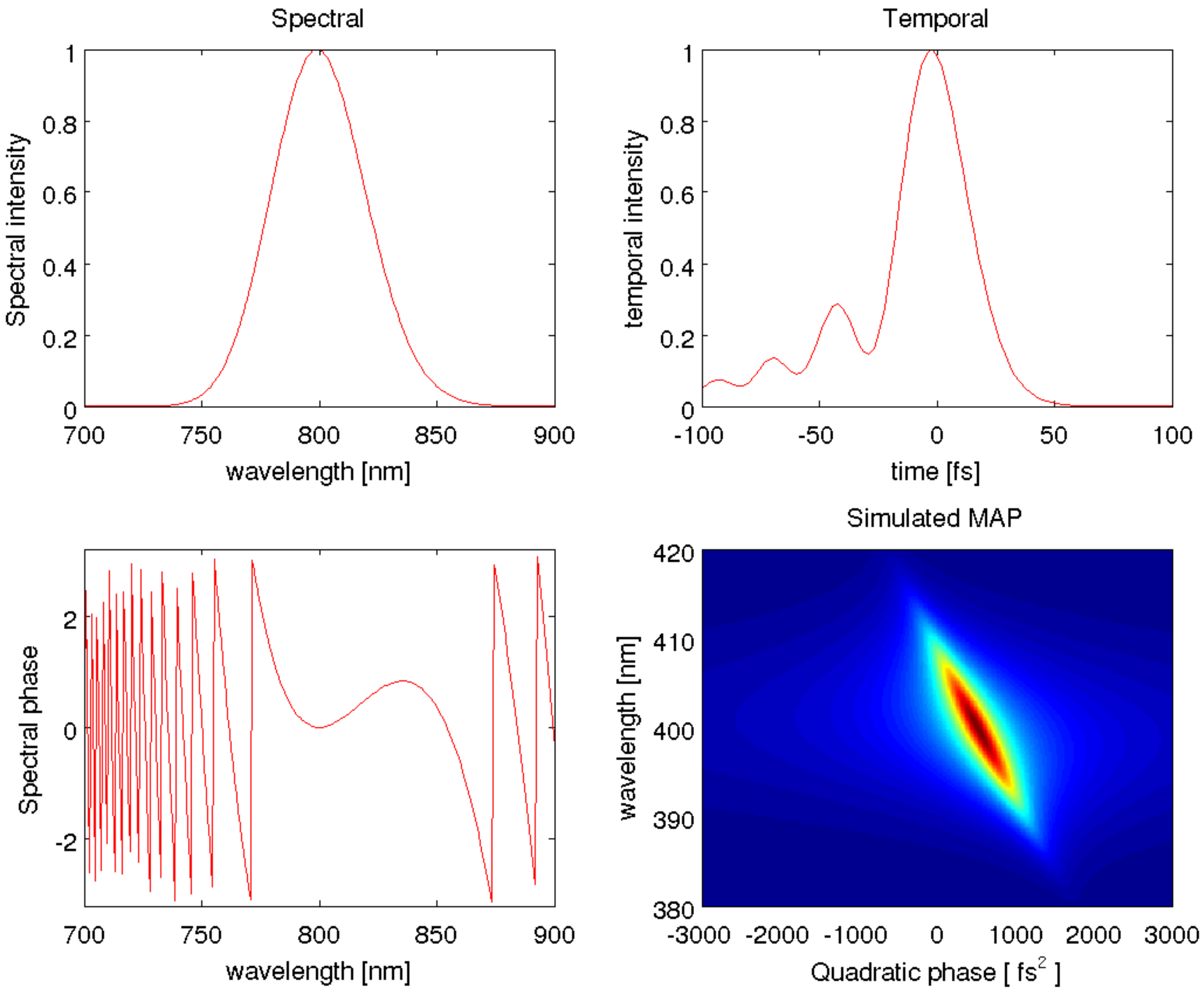
Toolbox – Pulse Measurement – Chirp Scan 500 fs²



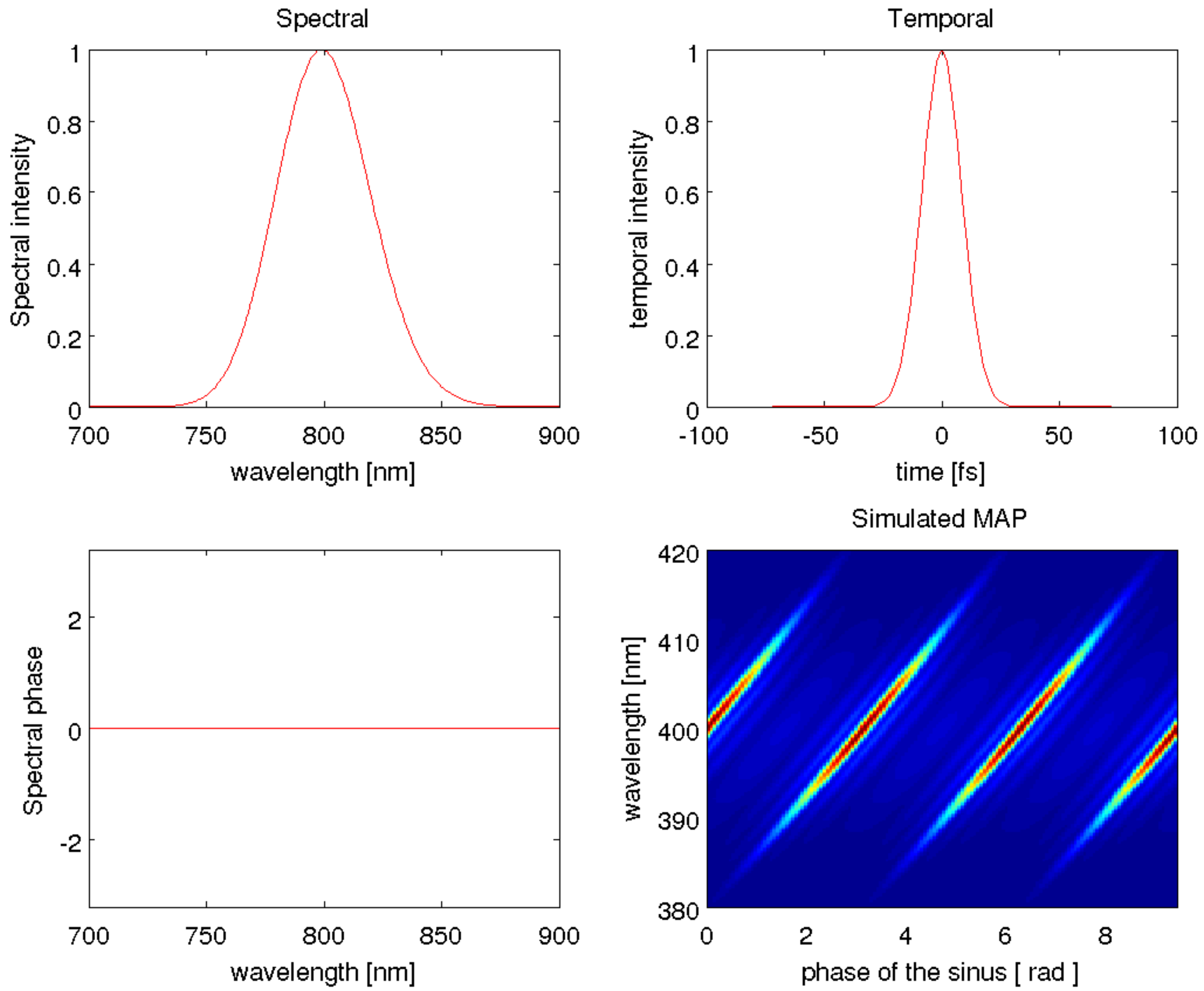
Toolbox – Pulse Measurement – Chirp Scan 20 000 fs^3



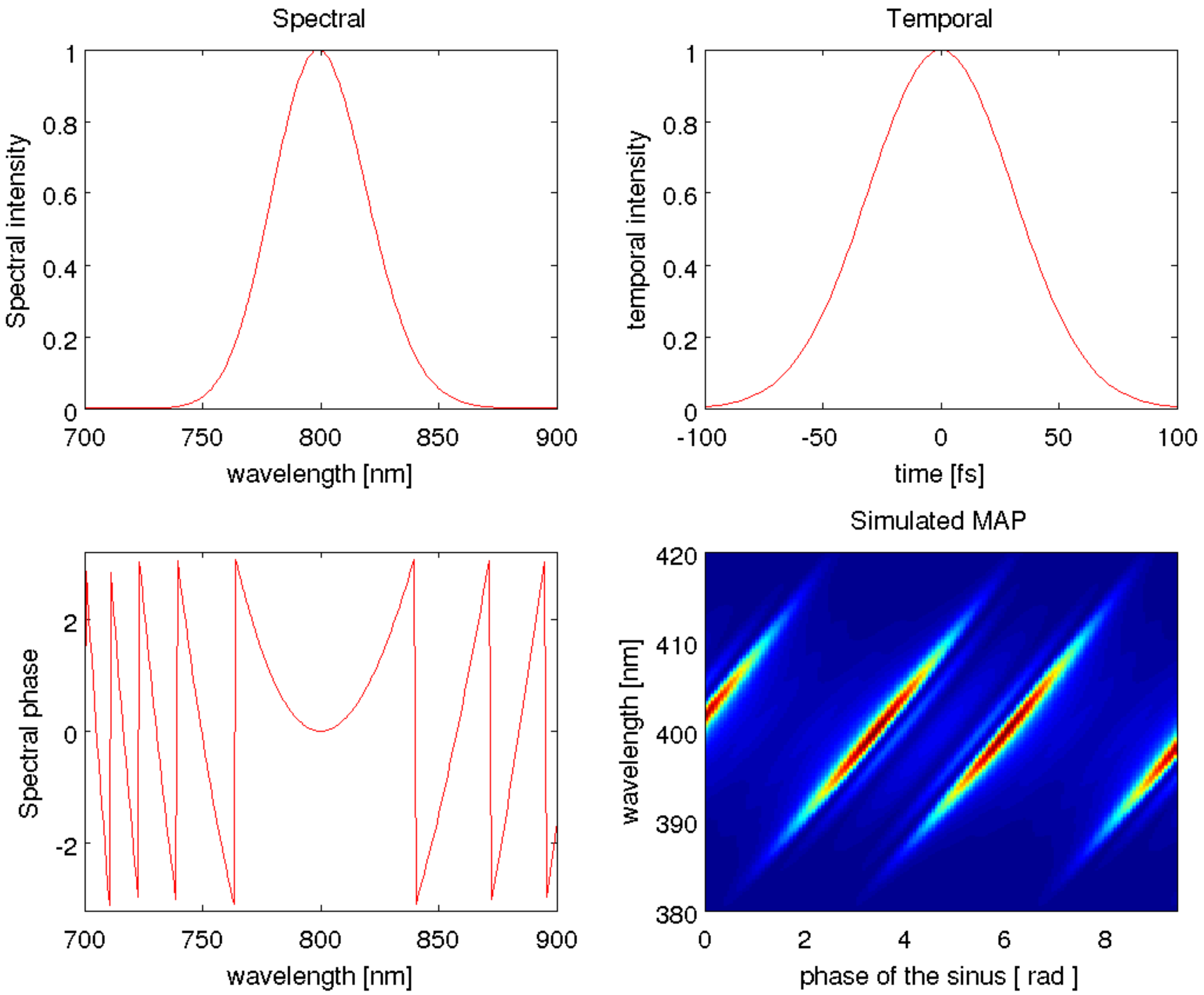
Toolbox – Pulse Measurement – Chirp Scan 500 fs² + 20 000 fs³



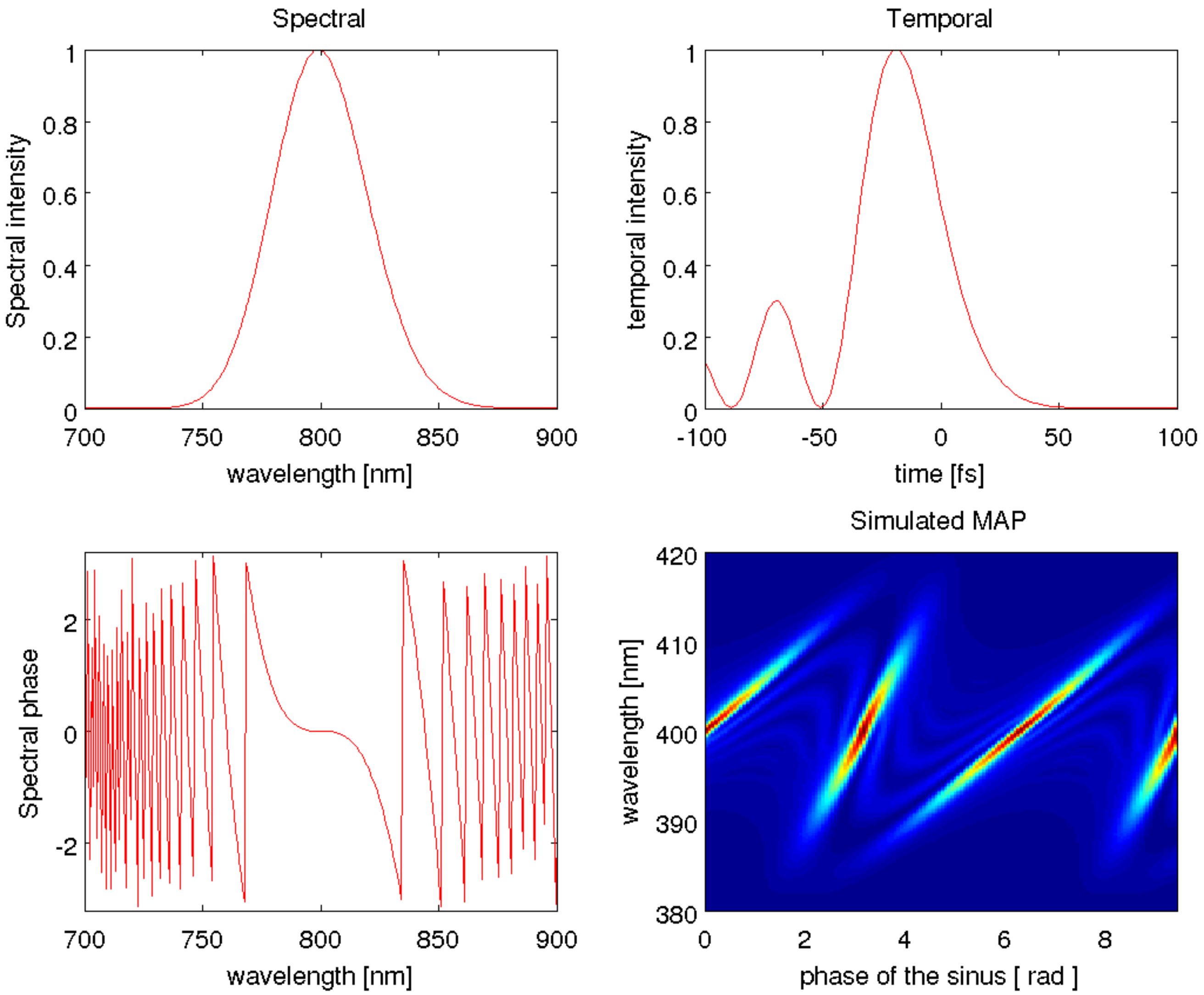
Toolbox – Pulse Measurement – MIIPS LFT



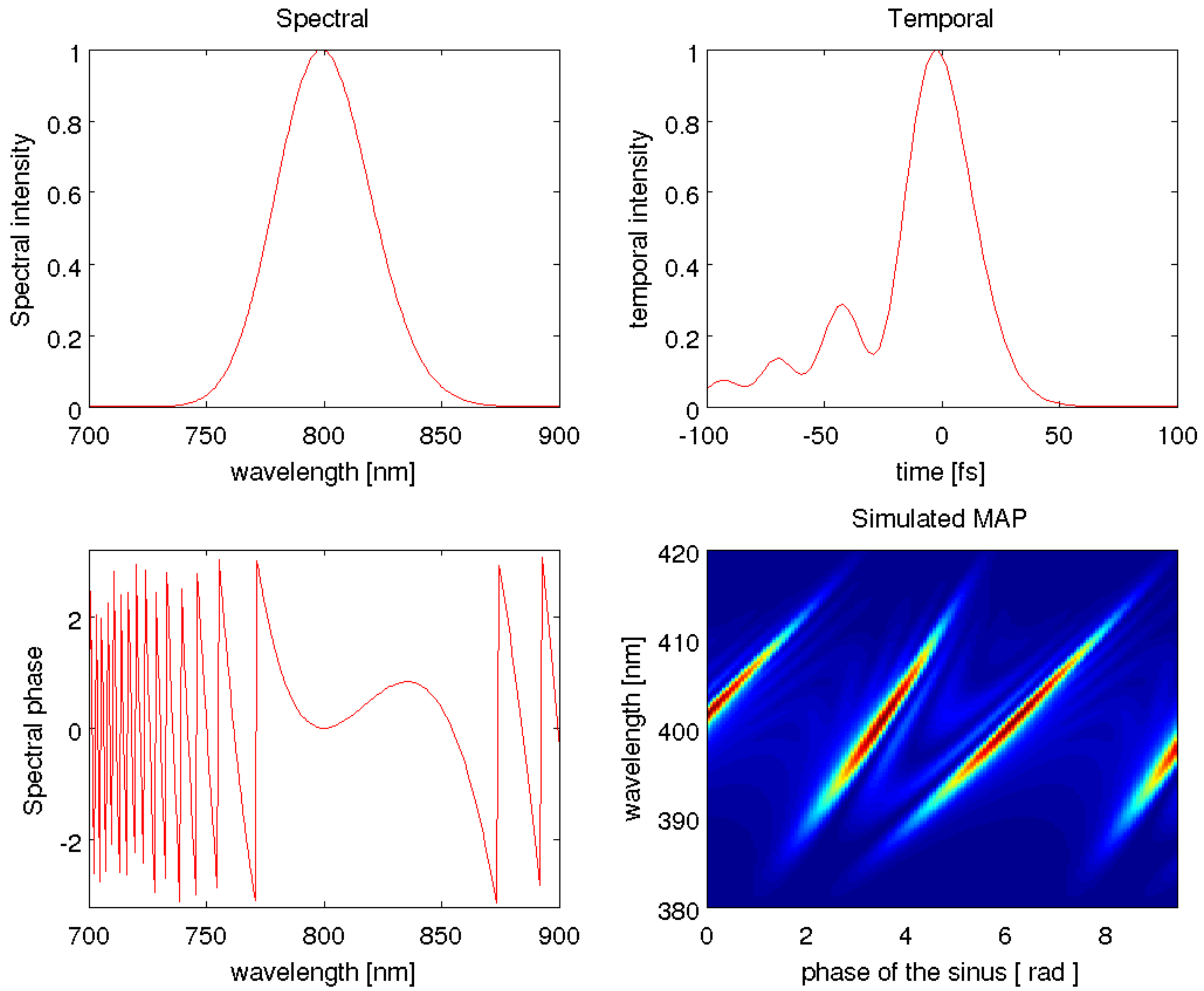
Toolbox – Pulse Measurement – MIIPS 500 fs²



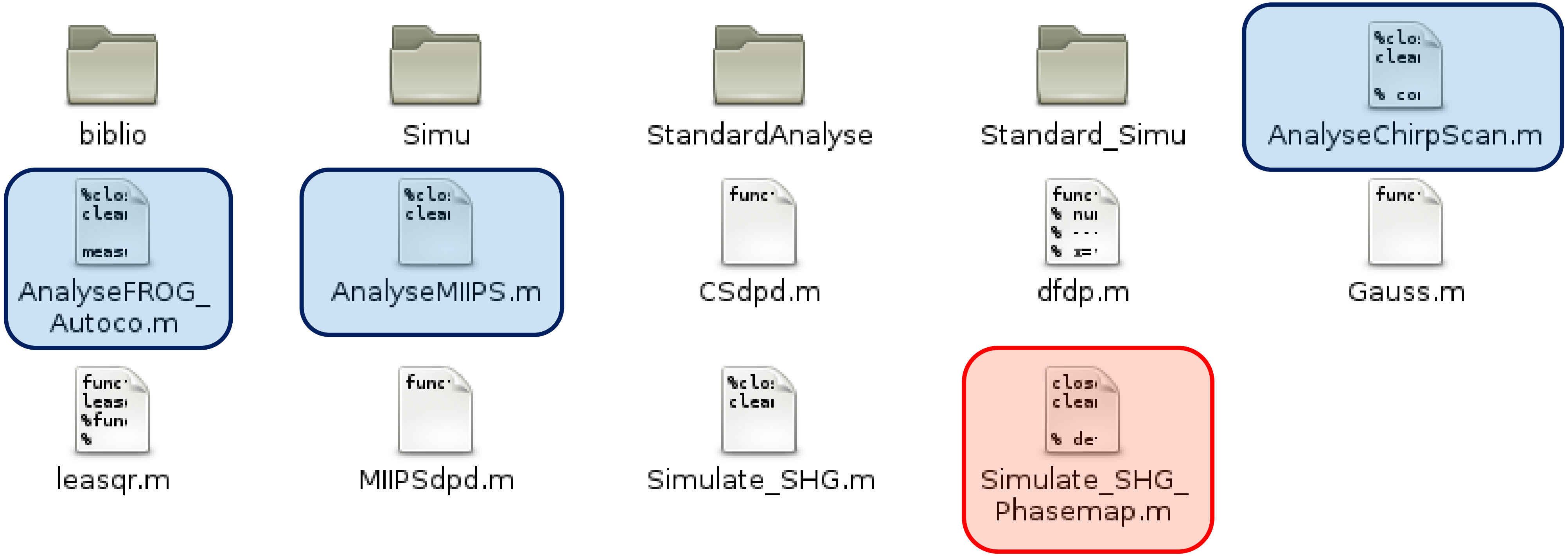
Toolbox – Pulse Measurement – MIIPS 20 000 fs^3



Toolbox – Pulse Measurement – MIIPS 500 fs² + 20 000 fs³



Toolbox – Pulse Measurement – Practice



http://frog.gatech.edu/code.html

https://github.com/xmhk/froglib

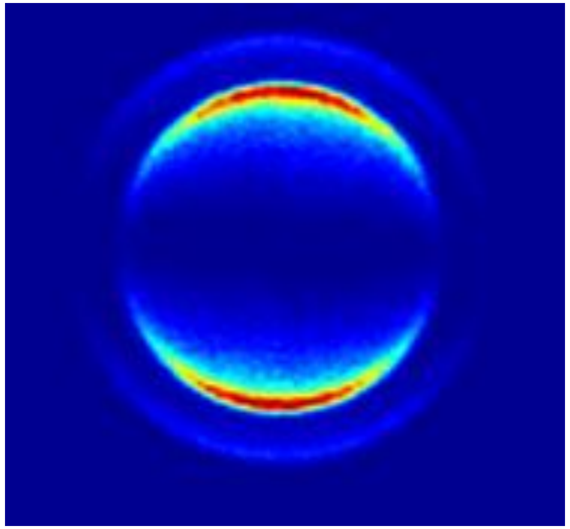
Chose the spectral properties of the pulse and simulate the S(2ω,p) map

- Get a feeling on the methods (sensitivity, different spectral amplitude an phase,…)
- Try to reconstruct the initial pulse with the “Analyse---.m” functions
- Test the robustness of the methods with different noise levels
- Introduce your own experimental measurement and interpret the result

Python code

Paul Hockett toolbox
acquisition & analysis
https://github.com/phockett/frogDAQ

Toolbox – Time Resolved Velocity Map Imaging



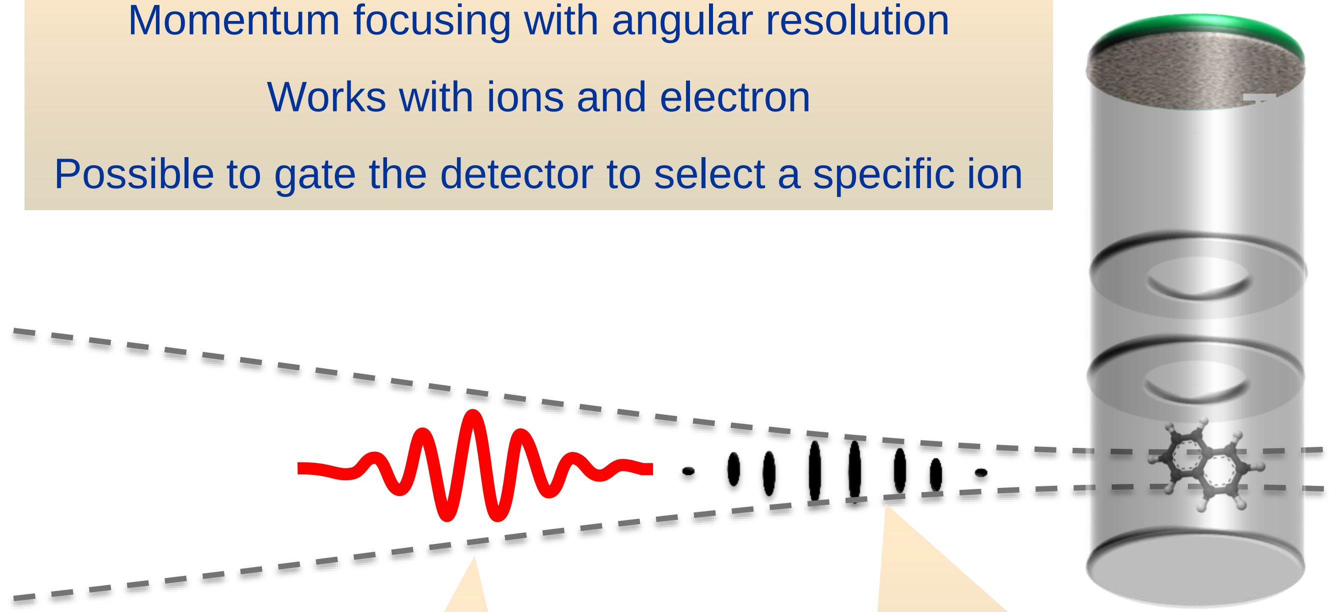
Toolbox – Time-resolved Velocity Map Imaging

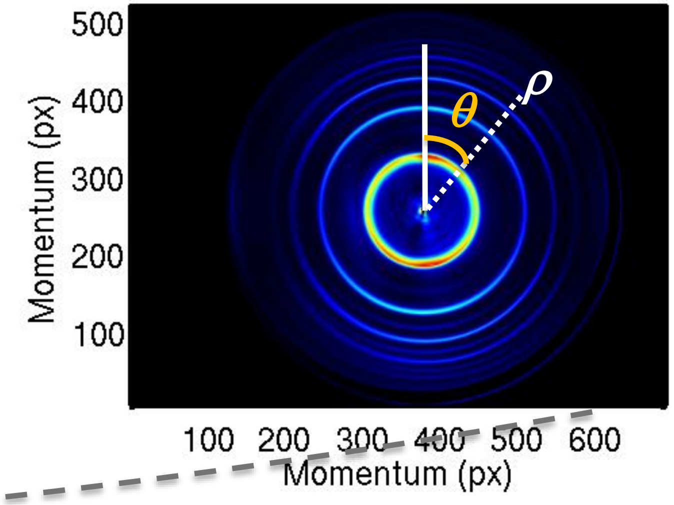
VMI : Velocity Map Imaging

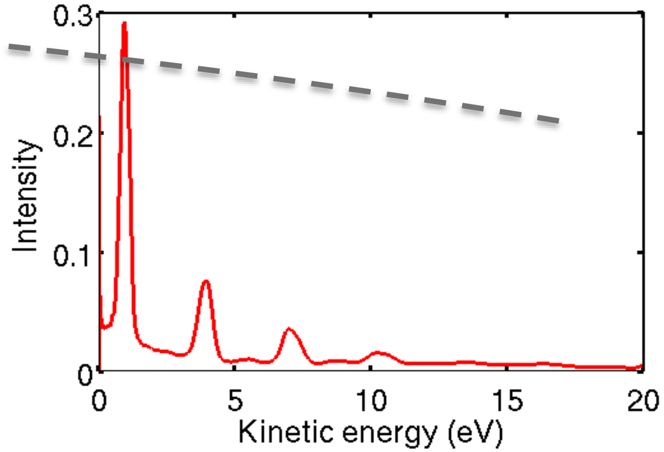
Momentum focusing with angular resolution

Works with ions and electron

Possible to gate the detector to select a specific ion







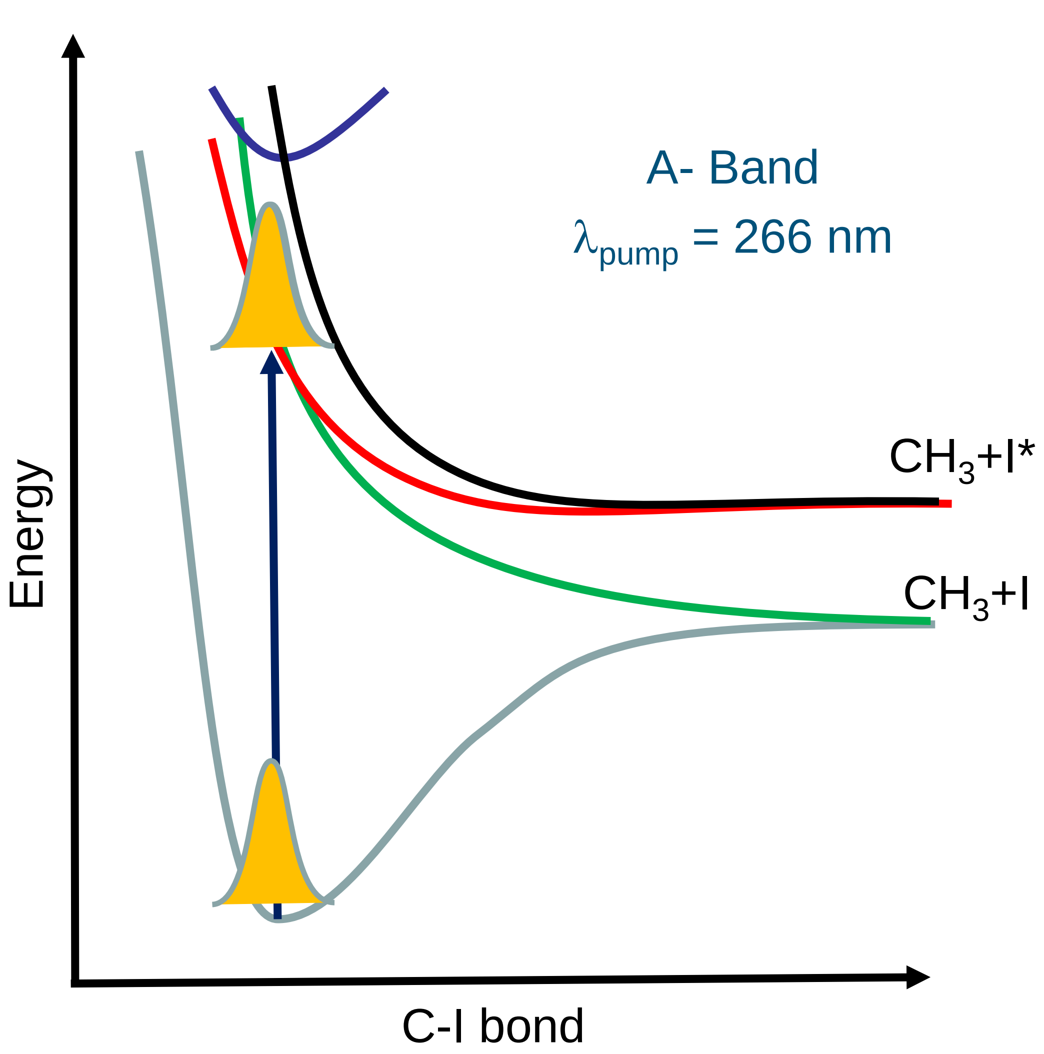
Pump pulse

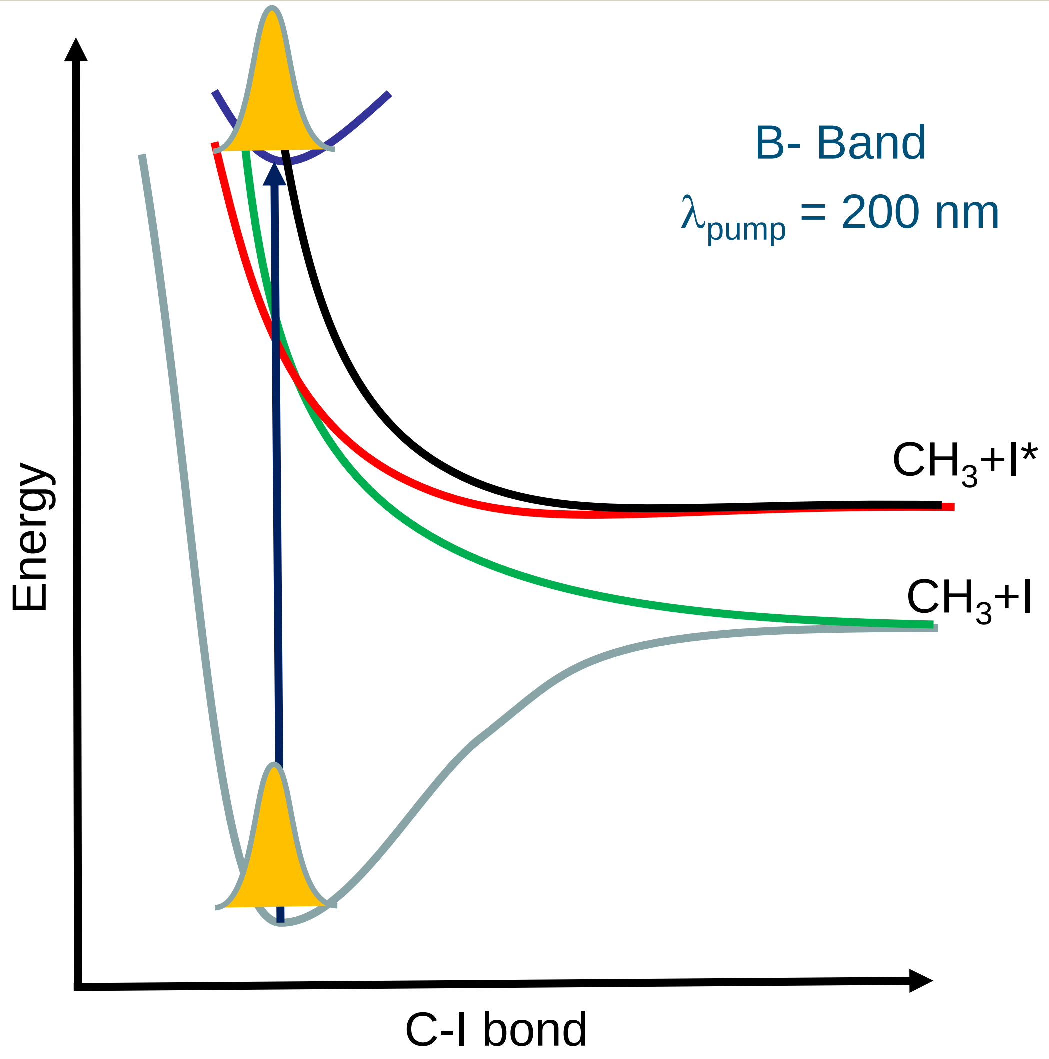
(Initiate a photo-reaction)

Probe pulse

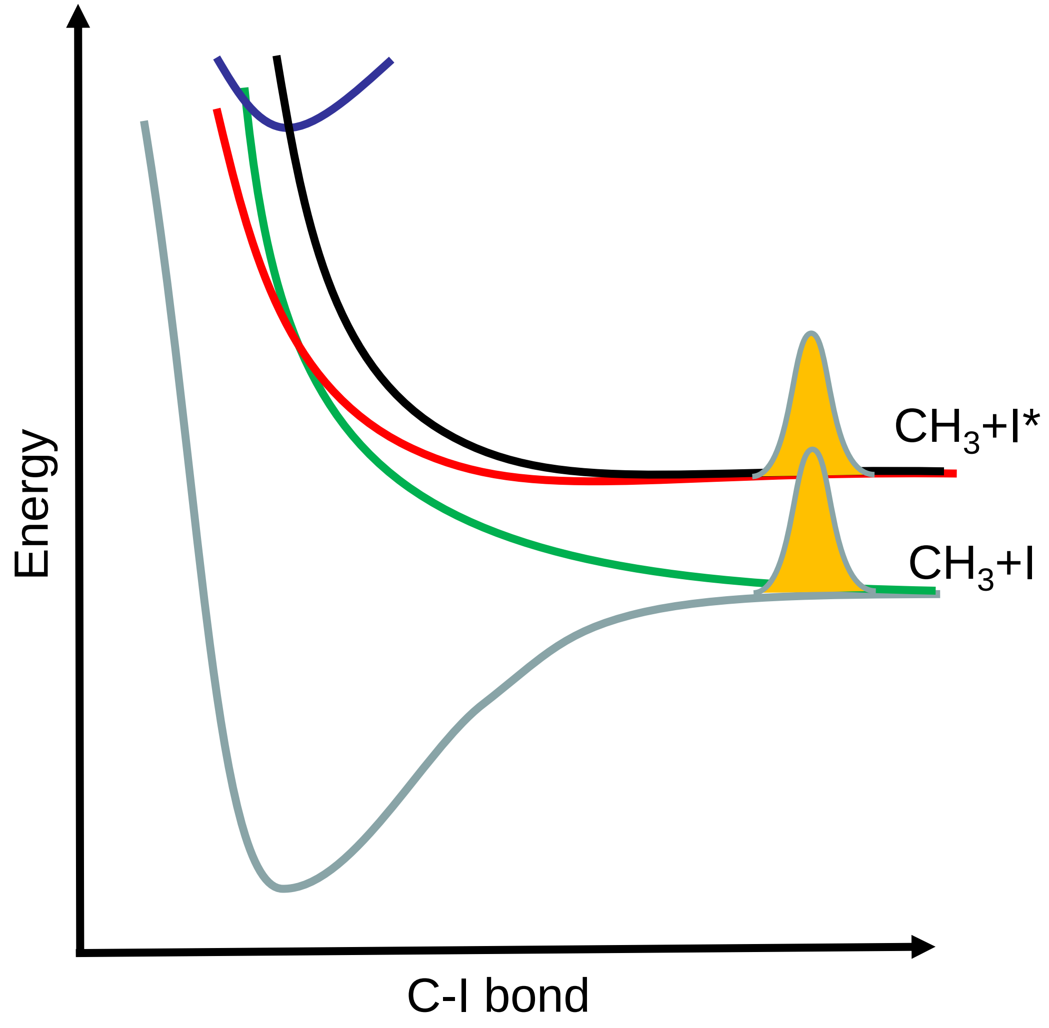
(measure the state of the system)

Toolbox – TR VMI – photodissociation of CH_3I





Toolbox – TR VMI – photodissociation of CH_3I



Measurement of CH_3 & Iodine fragments

Resonant (REMPI) detection of the fragments:

λ_{probe} = 333 nm -> CH_3

λ_{probe} = 305 nm -> Iodine

Kinetic energy of the fragments

Total kinetic energy :

Channel Iodine : $E_{tot} = E_{h\nu} - D_0$

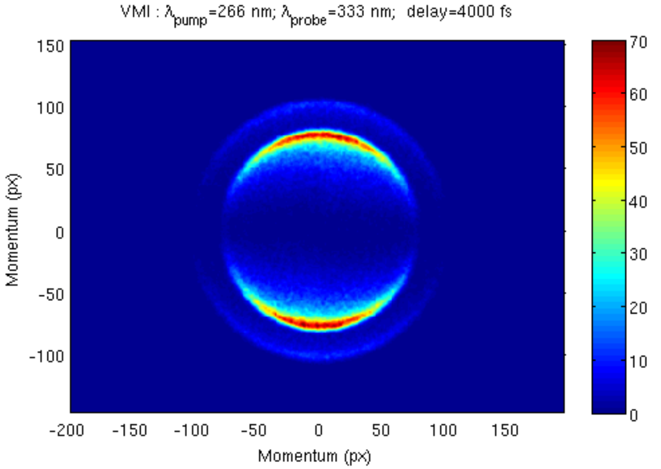
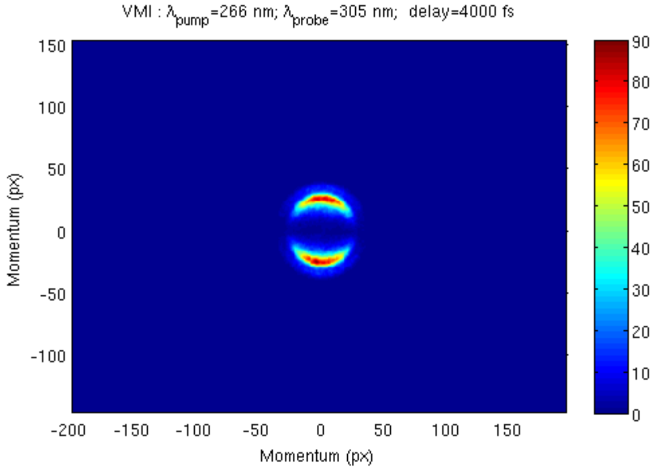
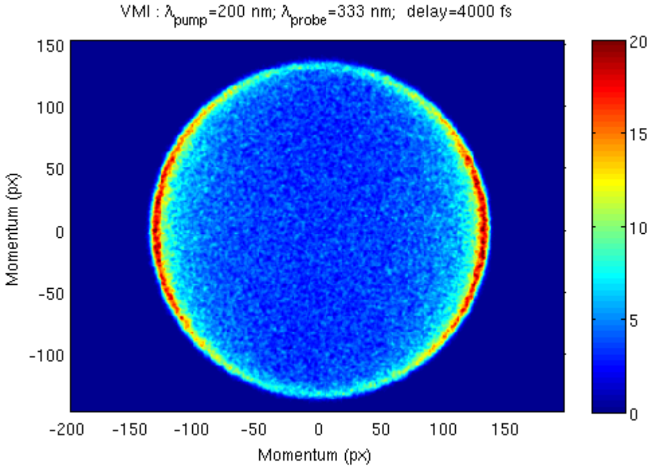
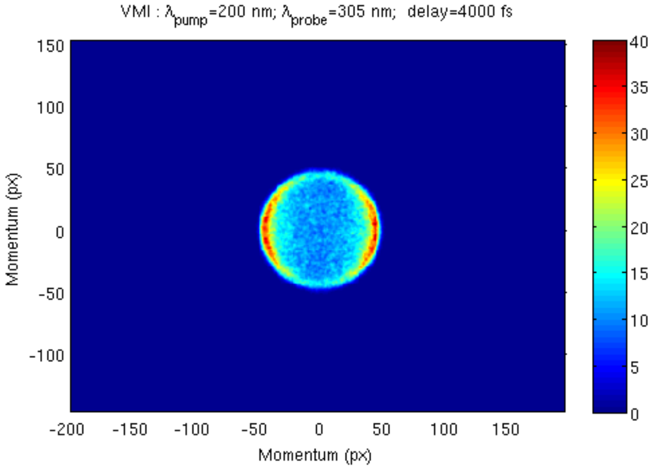
Channel Iodine : $E_{tot} = E_{h\nu} - D_0 - E_{so}$

Kinetic energy of a fragment:

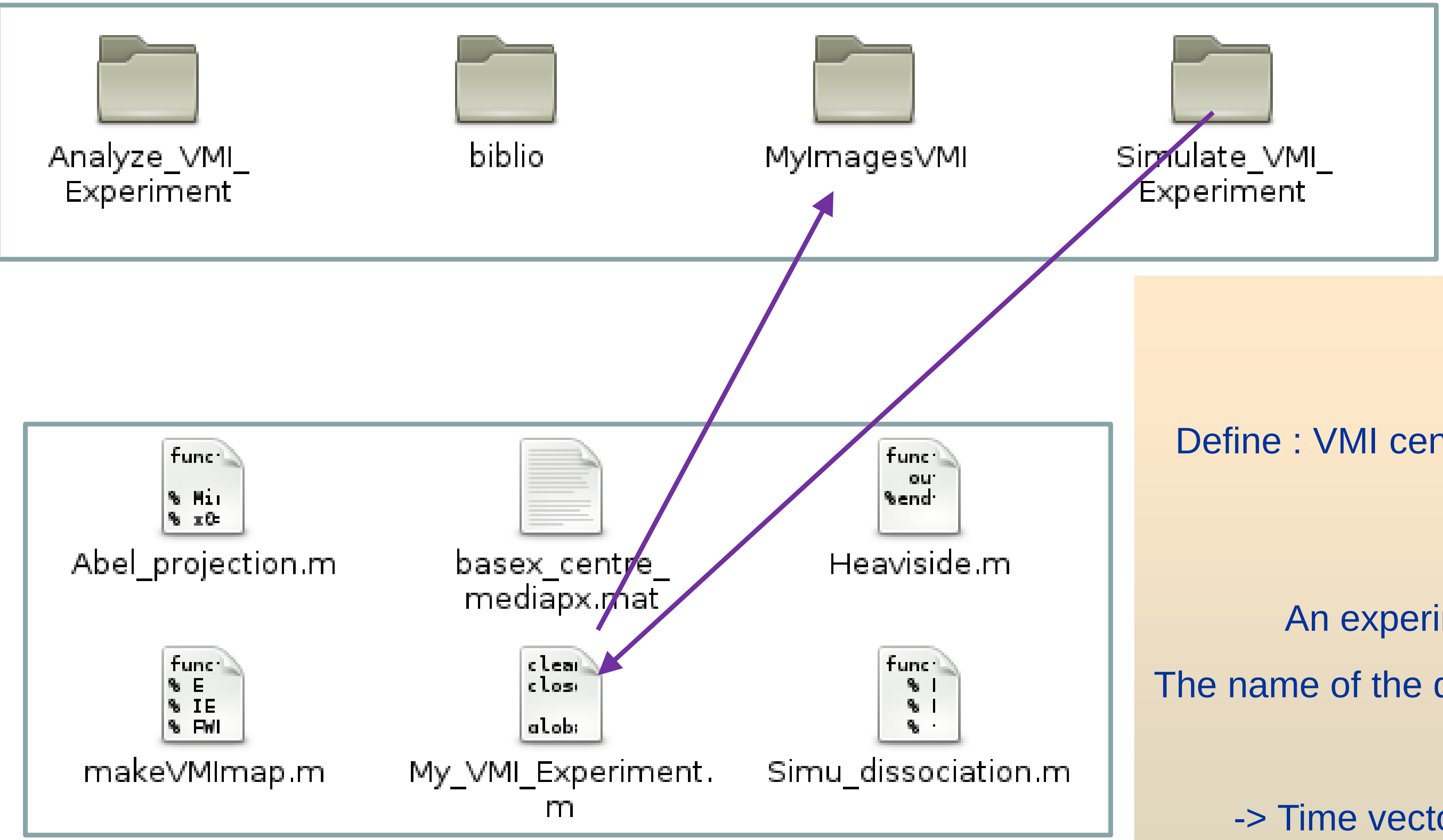
$E_{CH3} = m_I/m_{CH3I}$ Etot

$E_I = m_{CH3}/m_{CH3I}$ Etot

Toolbox – TR VMI – photodissociation of CH_3I End of the reaction

Detection	CH3 λ_{probe} = 333 nm	Iodine λ_{probe} = 305 nm
A- Band λ_{pump} = 266 nm		
B-Band λ_{pump} = 200 nm		

Toolbox – TR VMI – Simulate an experiment



Simulate an experiment

Define λ_{pump} and λ_{probe}

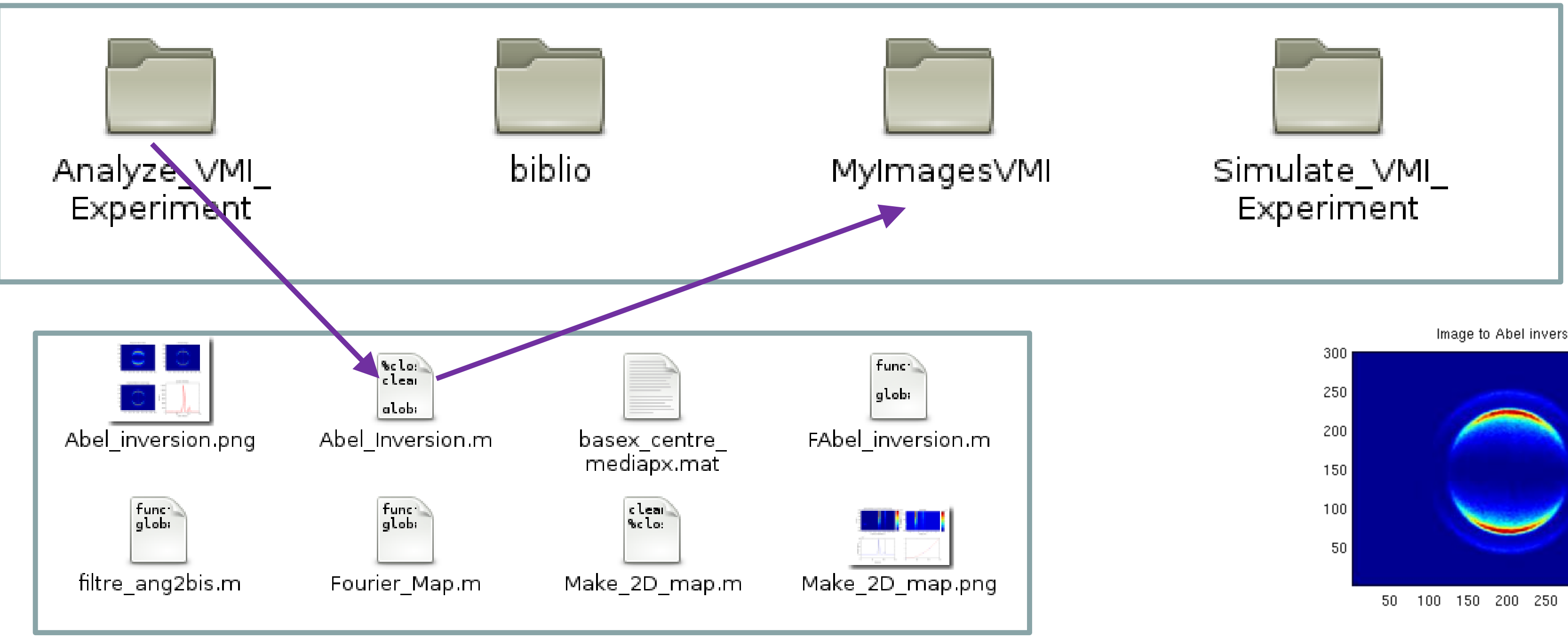
Define : VMI center, mean count event, delay vector (within for loop)

An experiment may appears in MyImagesVMI

The name of the directory is the λ_{pump} and λ_{probe}, day and time

-> Time vector is recorded and different VMI images according to the time vector

Toolbox – TR VMI – Abel inverse all image of the scan

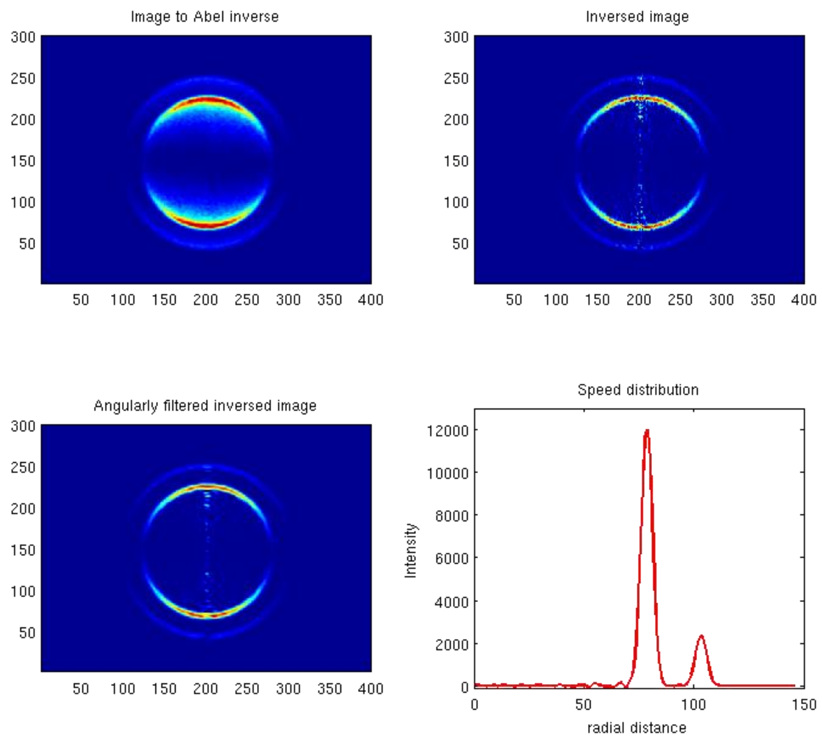


Abel inversion

Inverse image

Extract angular integration

Result written in the exp-directory



Abel inversion :

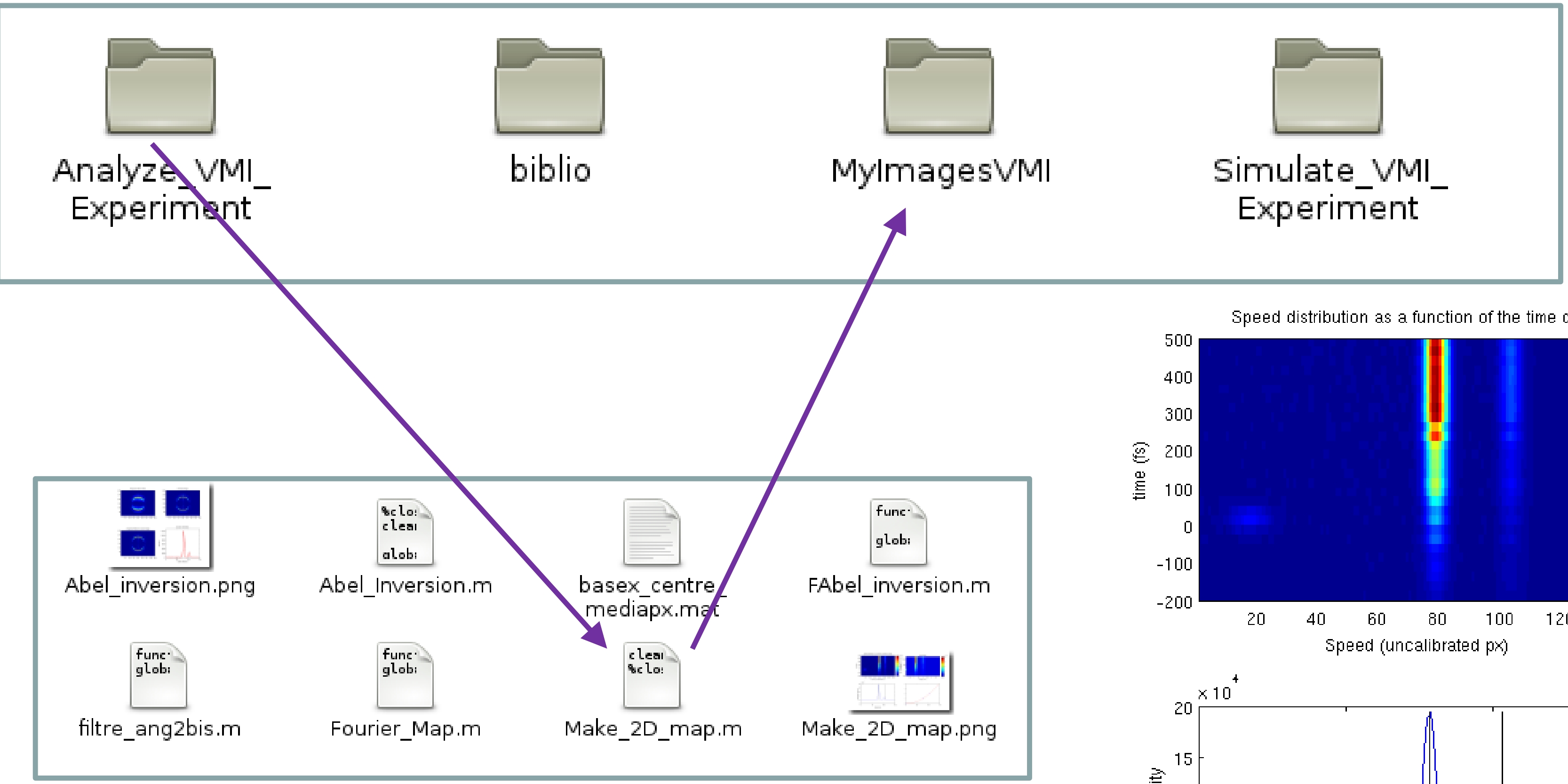
http://iramis.cea.fr/Phocea/file.php?class=cours&file=/lionel.poisson
/ICONIC_Freiburg_Lionel_POISSON_01.pptx

Pbasex Matlab : github.com/e-champenois/CPBASEX

Python : github.com/PyAbel

ExpToolbox

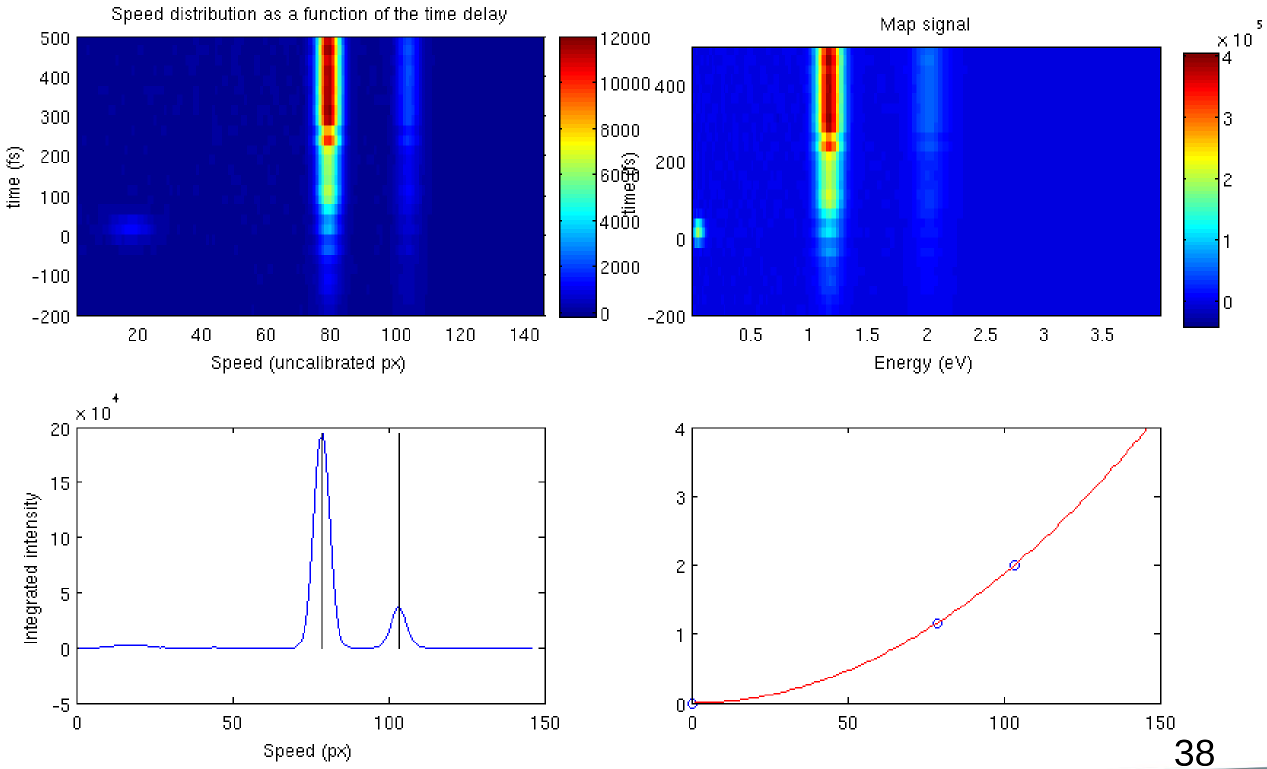
Toolbox – TR VMI – make the 2D map



<u>2D map</u>

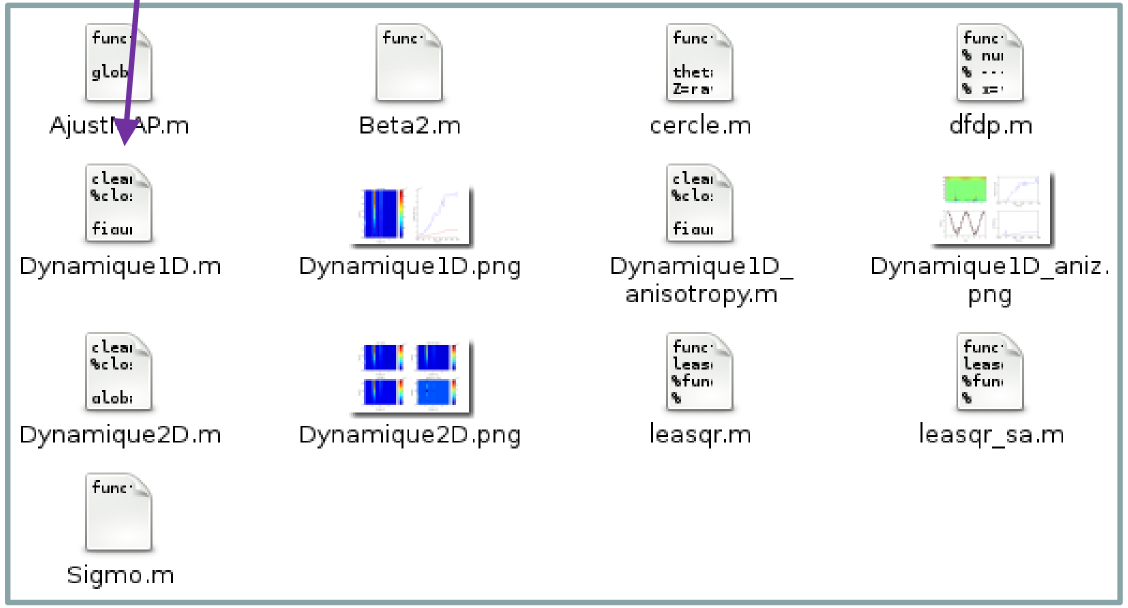
Make the map S(Kinetic energy, delay)

Calibrate the kinetic energy



ExpToolbox

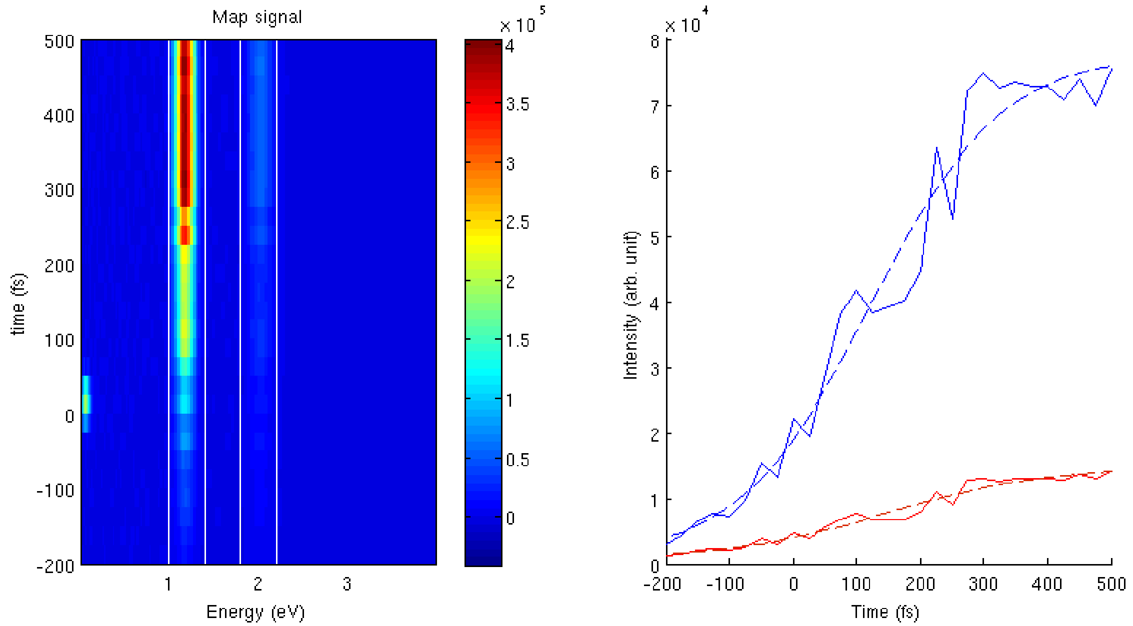
Toolbox – TR VMI – 1D temporal analysis



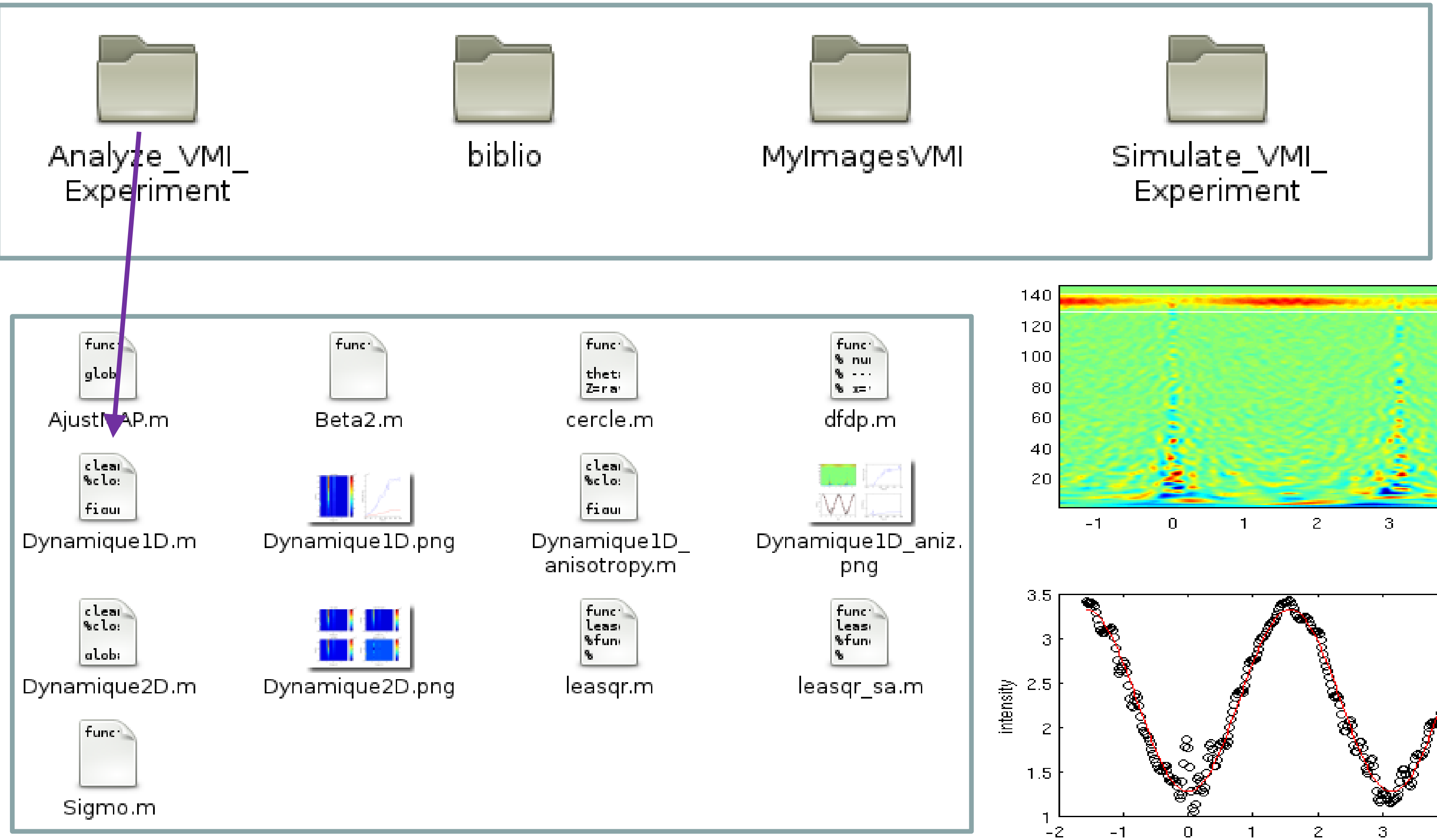
1D integration and fit

Integrate the KE signal for each delay

Fit this curve with the adapted signal

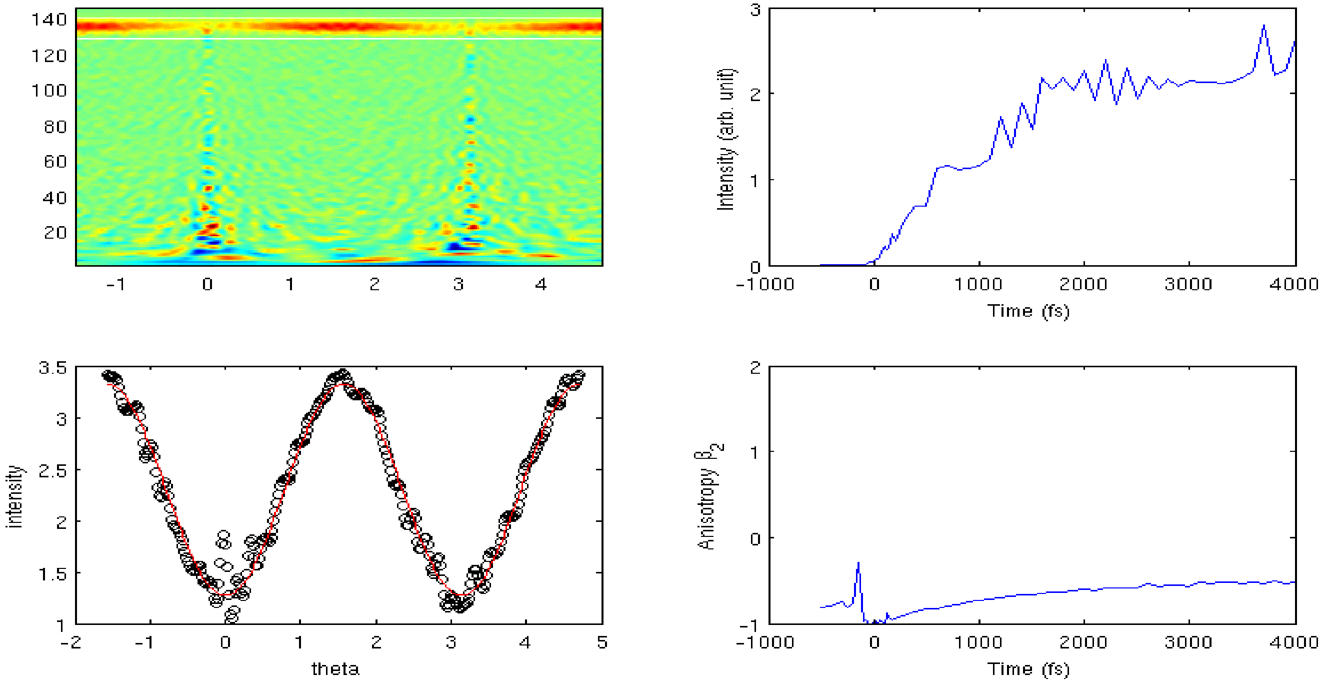


Toolbox – TR VMI – 1D temporal analysis anisotropy



1D integration and fit

Extract the anisotropy of a given contribution and plot it as a function of time



Toolbox – TR VMI – Practice

Simulate your own experiment

Modify the experimental parameters to get an feeling on the best parameters to acquire the experiment (VMI resolution, time-step, time limits, average, multiscan,…)

Analyse your experiment

Apply the Abel inversion, tune the best filter, test the effect of the resolution (test Pbasex ?)

Make your 2D maps with the best resolution possible

Analyze the data, modify the temporal expression if necessary

Justify the data observation

Use your own data

Outline

General framework for time-resolved acquisition

Drift of the parameters

General rule : Every parameter drifts in time

Different kind of drifts

Starting drift -> the warming up of the laser and electronics produce a drift up to the thermal gradient establishment (the first Hour)

Shot-to-shot reproducibility (ms scale)

Thermal fluctuation (minute timescale)

Weather fluctuation (humidity+ temperature)

Dust deposition-Chillers (week-month scale)

Long term miss-alignment (month/year scale)

Check your experimental parameters

Need to measure each parameter and its dependence in all the temporal timescale

Try to passively stabilize before active stabilization

Averaging / Sorting

Sorting : Do not record the data if the drift is too high

Averaging : if all the parameters slightly oscillates around their nominal value, average the acquisition over different timescales (multiscan).

Repeat the experiment different days

Storage of the information

ASCII TXT files

Compatible with any platform (Win/Mac/Linux)

Compatible with any analysis languages

Tab to separate the data always compatible

File name

May contain the year_month_day information

May contain the experiment kind (FROG,TR-VMI,…)

Sampling

Oversampling is not useful and needs a lot of space

The sampling is not the resolution!!

Undersampling does not measure well the experiment

Adapt your sampling step (regular/irregular)

Directory to save the data

It is always a good choice to save the data in a directory that carry/is the day of the experiment year_month_day

- Easy to locate from the lab-book
- Name easy to synthetize with analysis program (matlab/python)
- All the experiments done in the same conditions can be easily retrieved
- An automatic recording of the experimental easy-access experimental parameter (Gas target, temperature, pressure, pulse duration, wavelength,…) is always welcome

ExpToolbox

Storage of the data 0D, 1D and 2D in a single file

0D-1D signal

X1	Y1
X2	Y2
X3	Y3
X4	Y4
…	…

0D Photodiode
1D Spectrum
1D Time resolved photodiode

2D signal

0	Y1	Y2	Y3	Y4	…
X1	Z11	Z12	Z13	Z14	…
X2	Z21	Z22	Z23	Z24	…
X3	Z31	Z32	Z33	Z34	…
X4	Z41	Z42	Z43	Z44	…
…	…	…	…	…	…

2D 2x0D Time and wavelength resolved photodiode
2D 1x1D Time resolved spectral measurement
2D image

Storage of the data 3D to nD in a directory

Directory

Parameter 1.txt

A1
A2
A3
A4
…

2D signal A1

0	Y1	Y2	…
X1	Z11	Z12	…
X2	Z21	Z22	…
…	…	…	…

2D signal A2

0	Y1	Y2	…
X1	Z11	Z12	…
X2	Z21	Z22	…
…	…	…	…

nD as a function of :

- The time delay
- The pressure
- The temperature
- The chirp
- The intensity
- The wavelength
- …

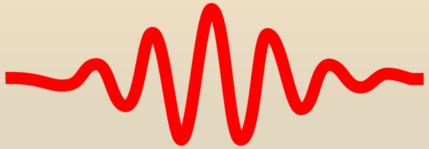
3D 3x0D Time, pressure and wavelength resolved photodiode
3D 2x1D Time and pressure resolved spectral measurement
3D 1x2D Time resolved image

Conclusion

- The data acquisition has to be carefully be done
- The noise treatment in the acquisition and in the analysis is a key point
- A periodic control / analysis of all the experimental parameters is very important
- The sampling has to be adapted
- The measurement storage system has to be simple and universal

TOOLBOX

Pulse measurement



Lets practice…

TOOLBOX

Time-resolved VMI