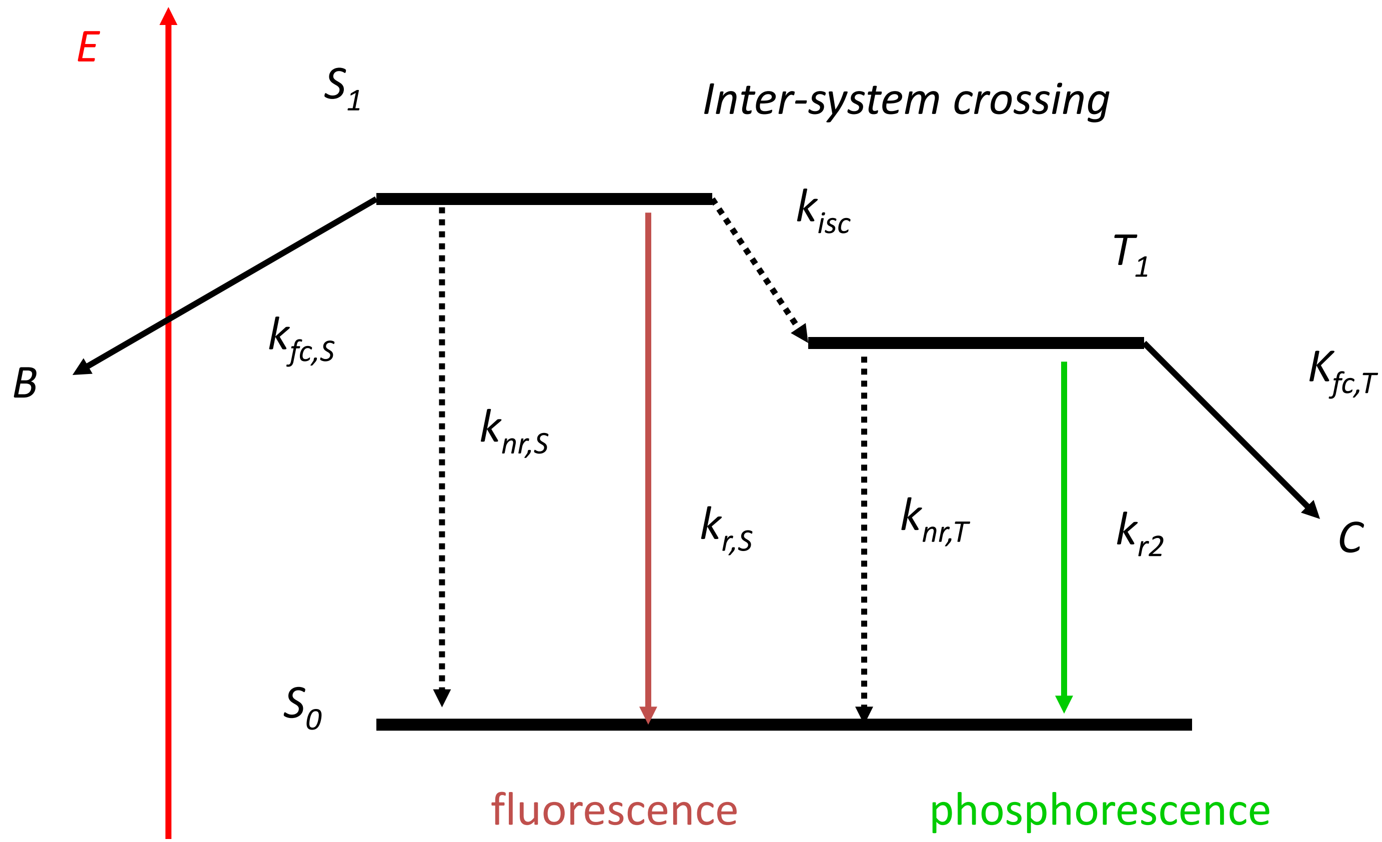
EXCITED STATE LIFETIME MEASUREMENTS

TIME CORRELATED SINGLE PHOTON COUNTING (TCSPC)

EXCITED STATE DEACTIVATION

(typical organic molecule)



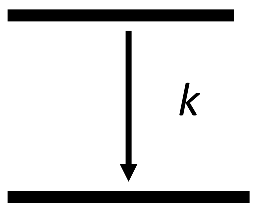
All these processes are uni-molecular with a first-order rate constant k

Excited state deactivation kinetics

*The "reactant" is an excited state: e.g. A**

In the case of a single process with rate constatn k:

$$\boxed{d[A^*]/dt = -k\,[A^*]}$$



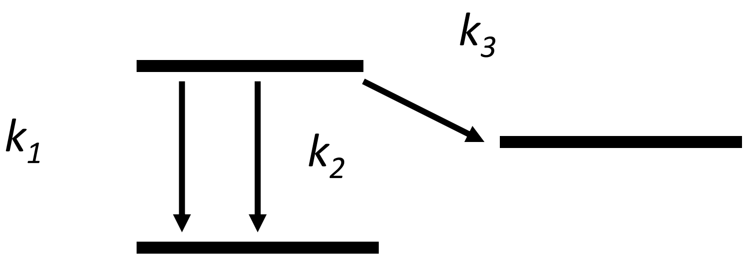
After integration:

$$\boxed{[A^*]=[A^*]_0 \exp(-kt)}$$

This means that if the excited state A is formed immediately (pulsed excitation) with a starting concetration* $[A^*]_0$ *this decays exponentially during time*

Excited state deactivation kinetics

*In the case of more **parallel** deactivation processes*



$$d[A^*]_1/dt = -k_1\,[A^*]$$

$$d[A^*]_2/dt = -k_2\,[A^*]$$

....

$$d[A^*]/dt = -(k_1 + k_2 + \ldots.)\,[A^*] = -\Sigma_i k_i\,[A^*]$$

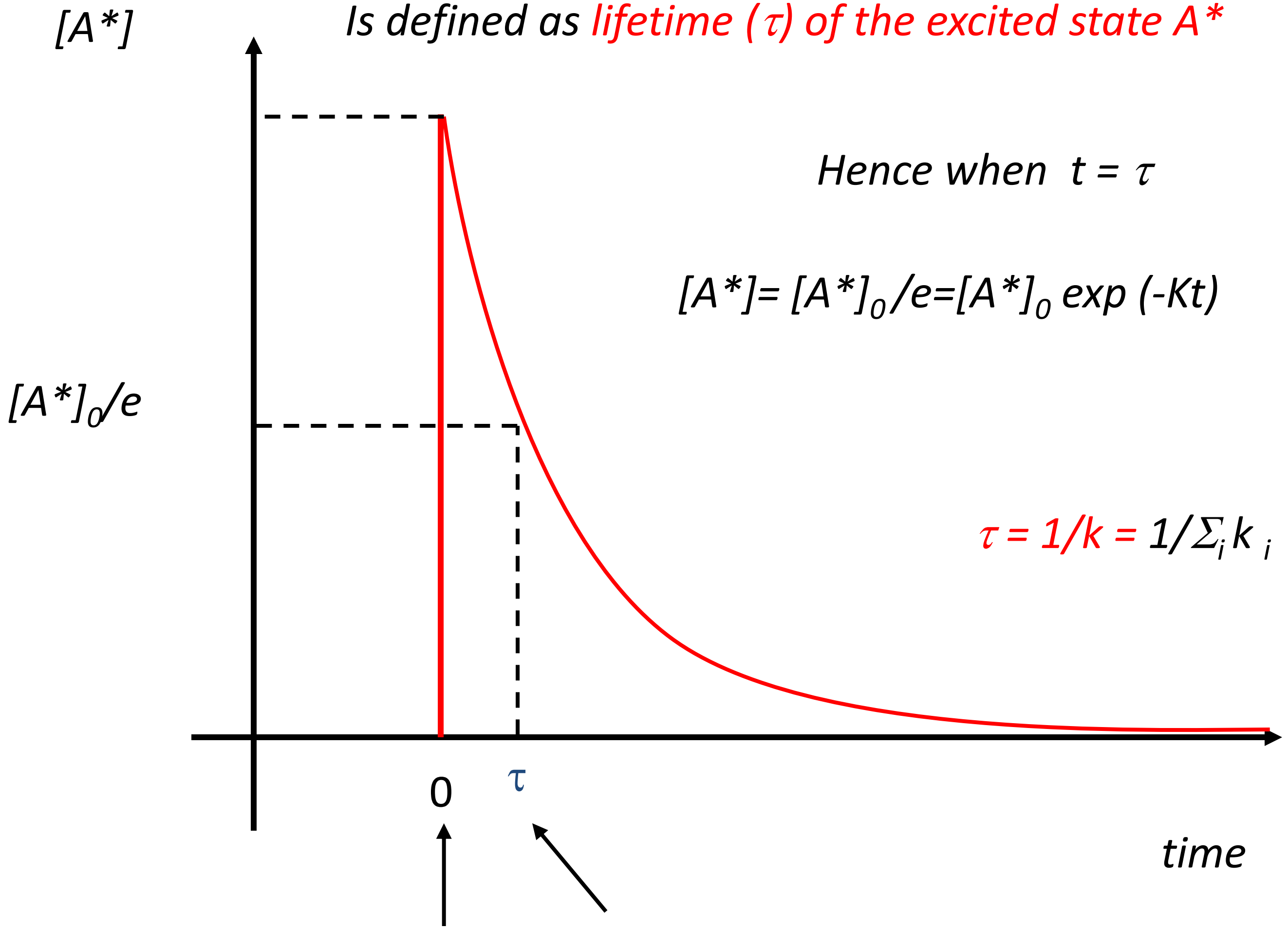
$$[A^*] = [A^*]_0 \exp\,(-\,\Sigma_i k_i\,t)$$

$$I(t) = d[A^*]_{rad}/dt = k_{rad}\,[A^*]_0 \exp\,(-\,\Sigma_i k_i\,t)$$

The system deactivates with the same exponential kinetics with an overall first-order rate constant $K=\Sigma_i k_i$

What is excited state lifetime

The value of time at which the concentration $[A^*]_0$ becomes $[A^*]_0/e$
Is defined as lifetime (τ) of the excited state A*



Hence when $t = \tau$

$$[A^*] = [A^*]_0/e = [A^*]_0 \exp(-Kt)$$

$$\tau = 1/k = 1/\Sigma_i k_i$$

Exciteation pulse: excited state is formed at concetration $[A^*]_0$

Excited state lifetime

Excited state deactivation kinetics (case of two emitting species)

$d[A^*]_1/dt = -k_{1,A}\,[A^*]$

$d[A^*]_2/dt = -k_{2,A}\,[A^*]$

....

$d[B^*]_1/dt = -k_{1,B}\,[B^*]$

$d[B^*]_2/dt = -k_{2,B}\,[B^*]$

....

$$dI/dt=-\alpha d[A^*]/dt - \beta d[B^*]/dt$$

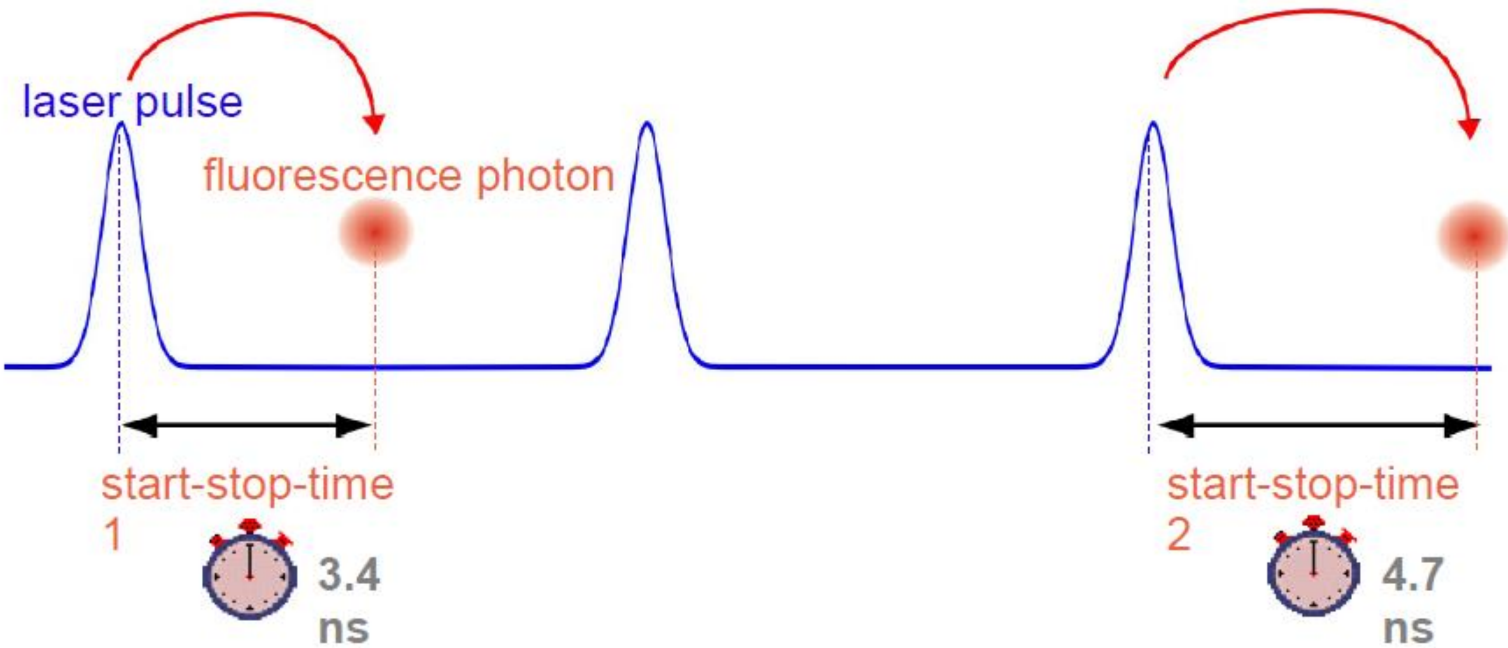
$$d[A^*]/dt = (k_{1,A} + k_{2,A} + \ldots.)\,[A^*] = -\Sigma_i k_{i,A}\,[A^*]$$

$$d[B^*]/dt = (k_{1,B} + k_{2,B} + \ldots.)\,[B^*] = -\Sigma_i k_{i,B}\,[B^*]$$

$$dI/dt=\alpha\,[A^*]_0 \exp(-t/\tau_A) + \beta\,[B^*]_0 \exp((-t/\tau_B)$$

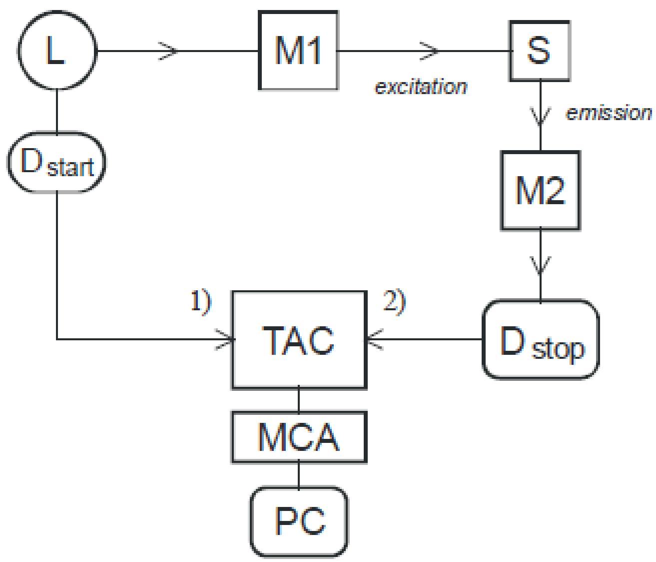
The decay is bi-exponential

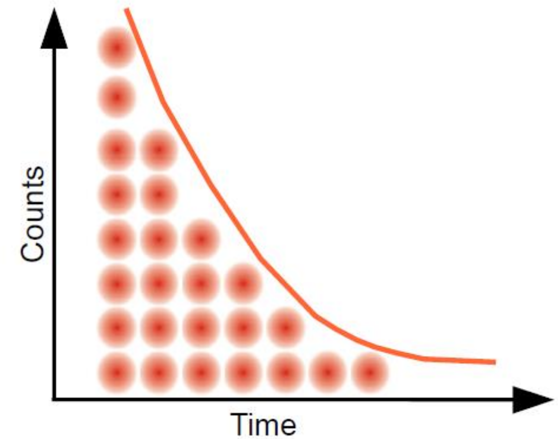
TIME CORRELATED SINGLE PHOTON COUNTING



Pulsed lamp based system

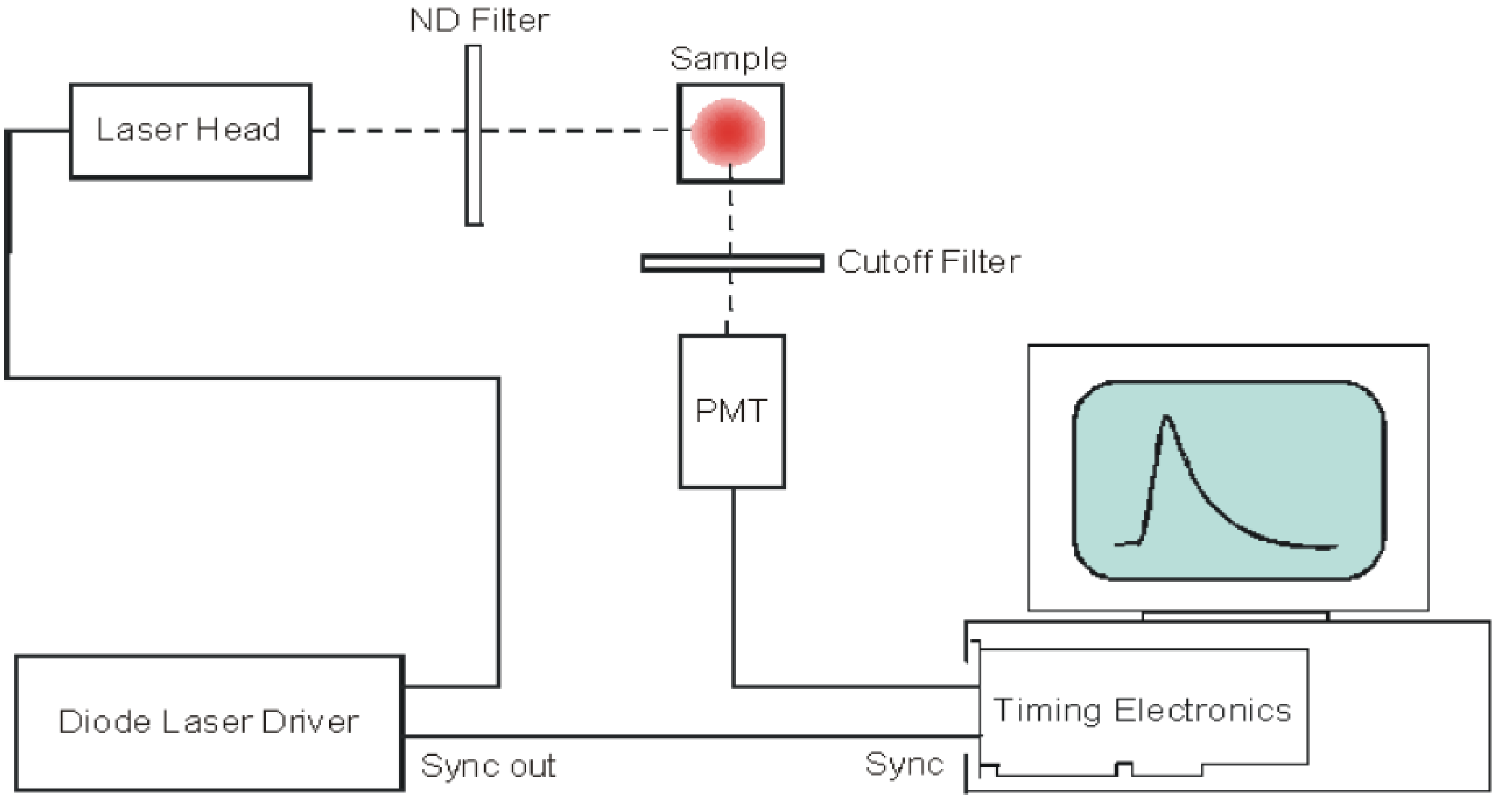
TIME-CORRELATED SINGLE-PHOTON COUNTING
ns time domain



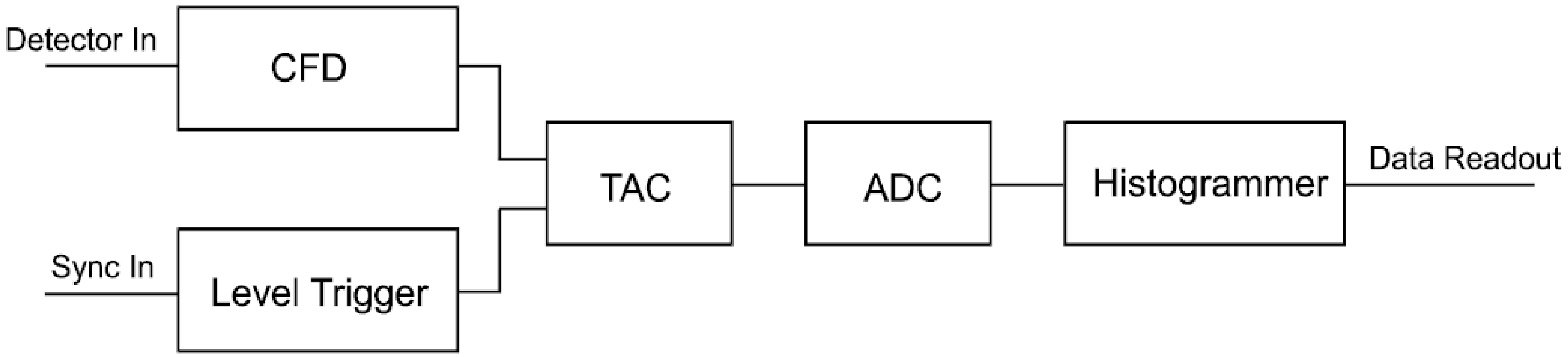


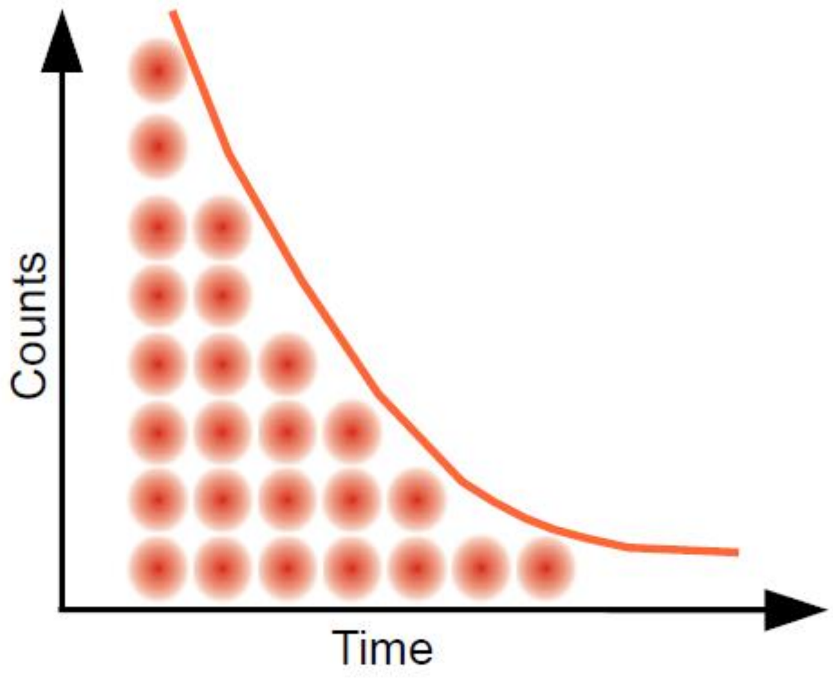
L = gas-filled arc flashlamp
M1 = excitation monochromator
S = sample
M2 = emission monochromator
Dstart = start detector
Dstop = stop detector
TAC = timebase unit
MCA = multichannel analyzer

PULSED LASER BASED TCSPC

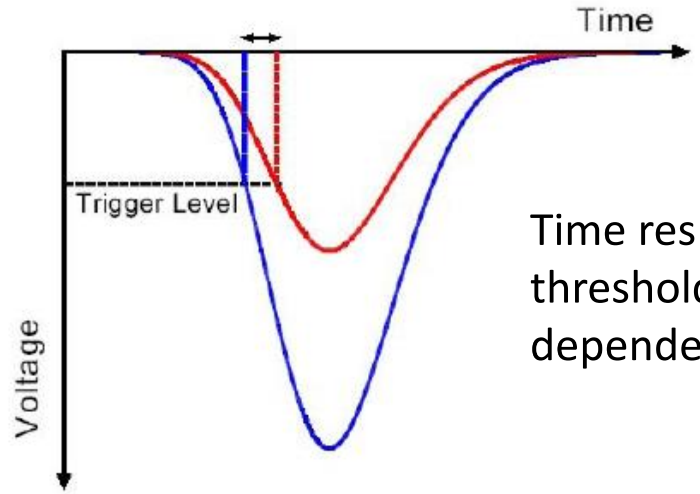


SCHEME OF THE ACQUISITION CARD



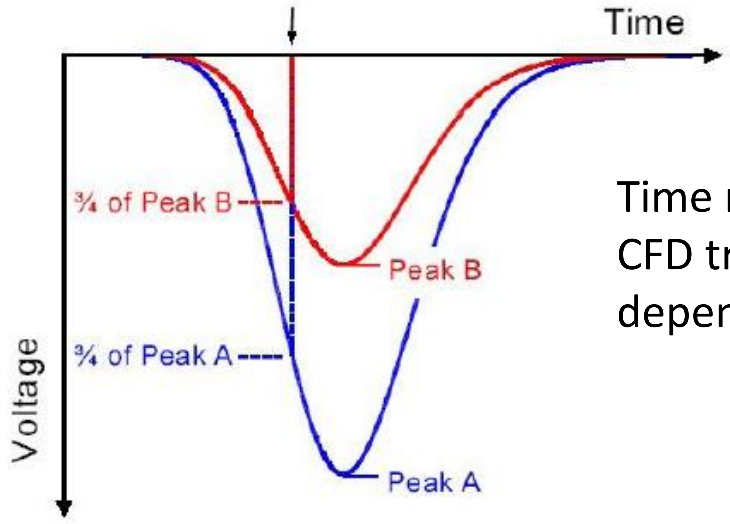


CFD: CONSTANT FRACTION DISCRIMINATOR



Time response of the threshold trigger is dependent on the intenity

Fig. 4: Constant level trigger



Time response of the CFD trigger is not dependent on the intenity

TIME CORRELATED SINGLE PHOTON COUNTING

The excitation source is selected considering the absorption properties .

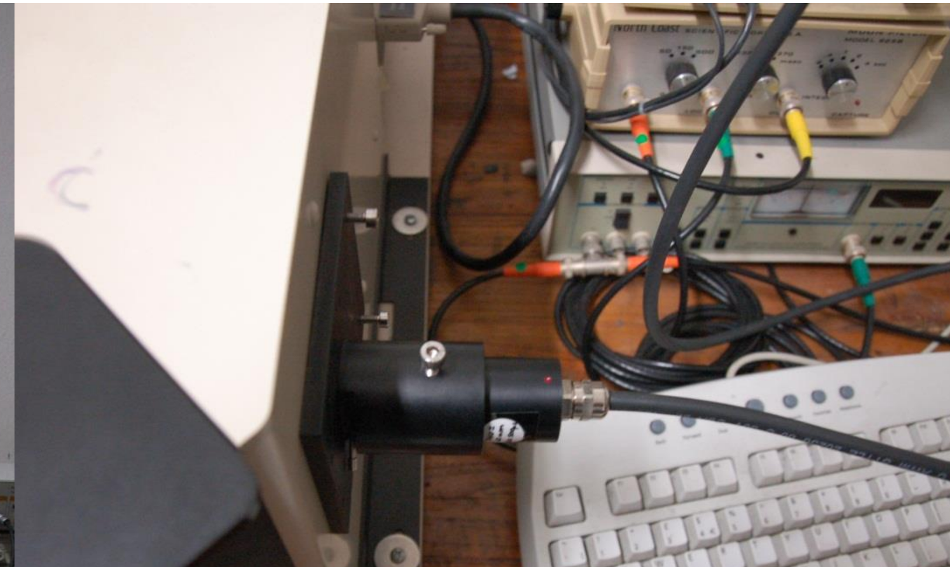
Soruces LASER DIODE: 405 nm
LED: 280 nm

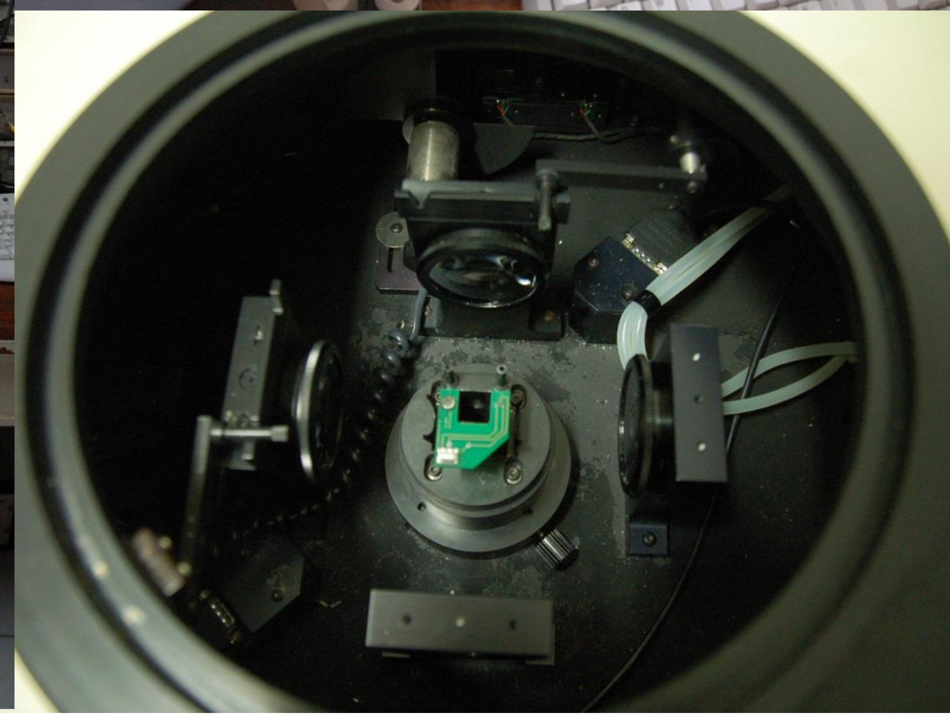
The controller frequency is adjusted so that the distance between two pulses is much greater (at least 10 times) than the life time

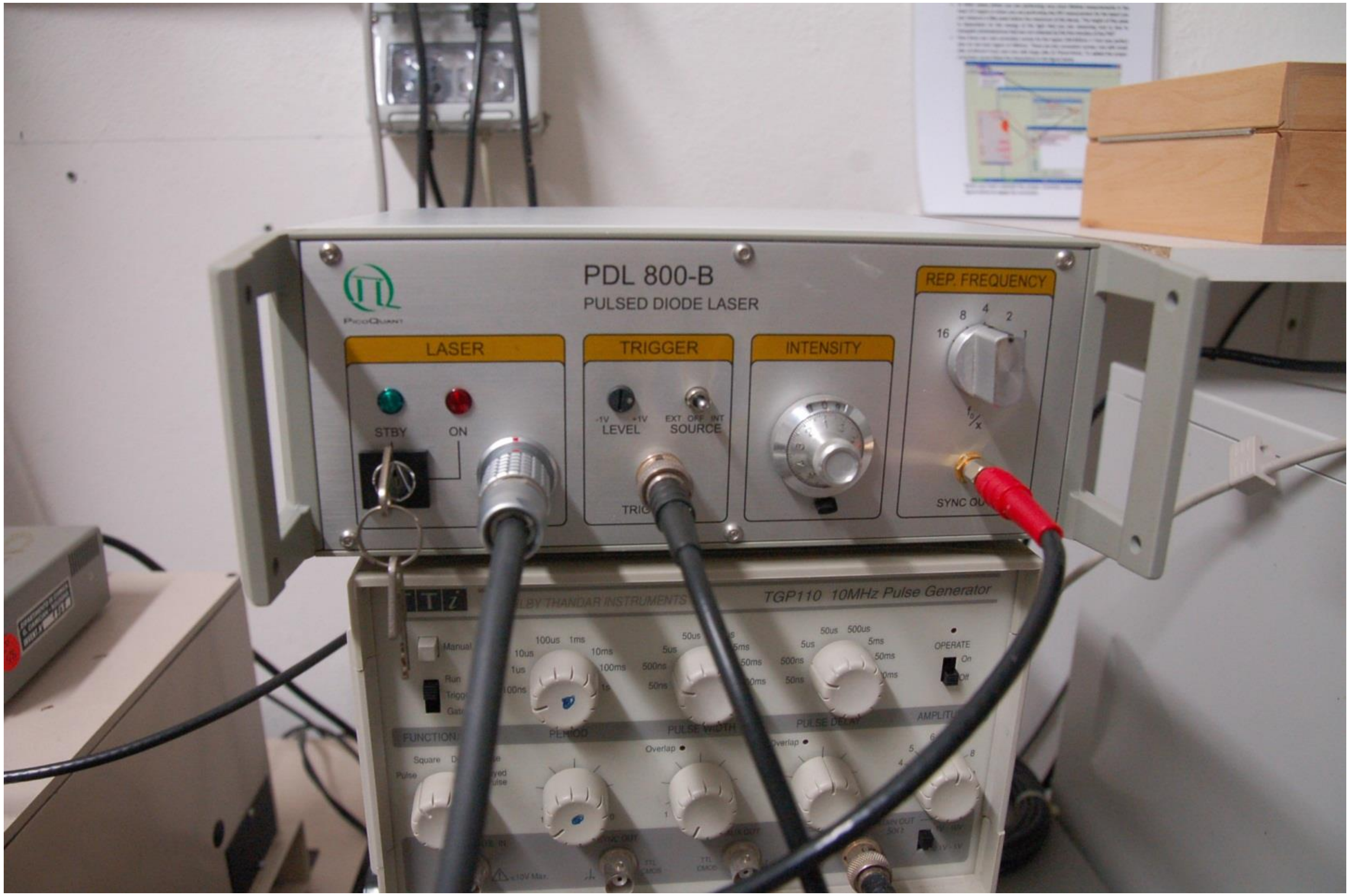
Frequenza (MHz)	40	20	10	5	2.5
Δt	25	50	100	200	400

The frequency indicates the number of pulses per second so the distance between two successive pulses is:

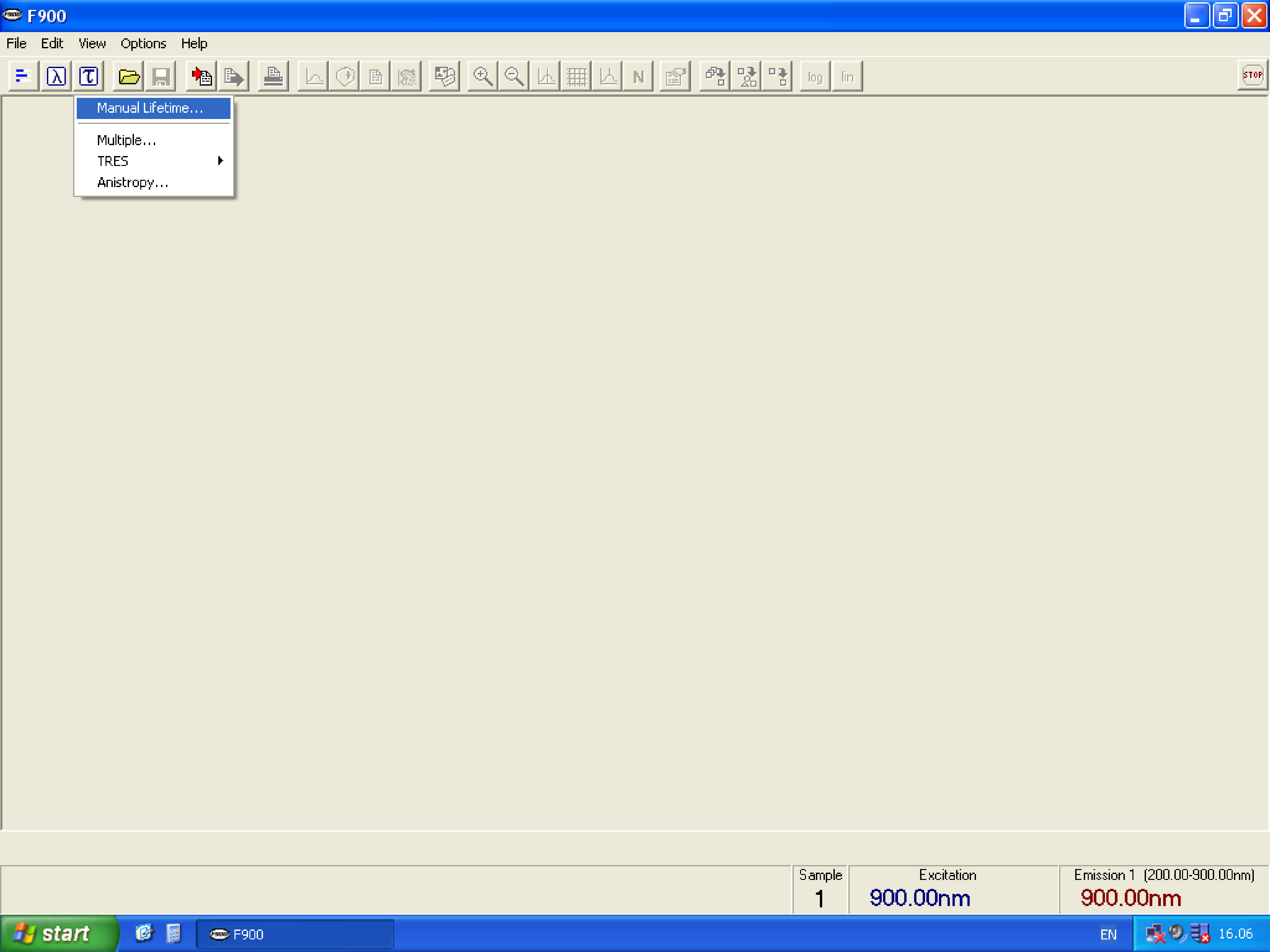
$$\Delta t = 1000(ns)/f(MHz)$$

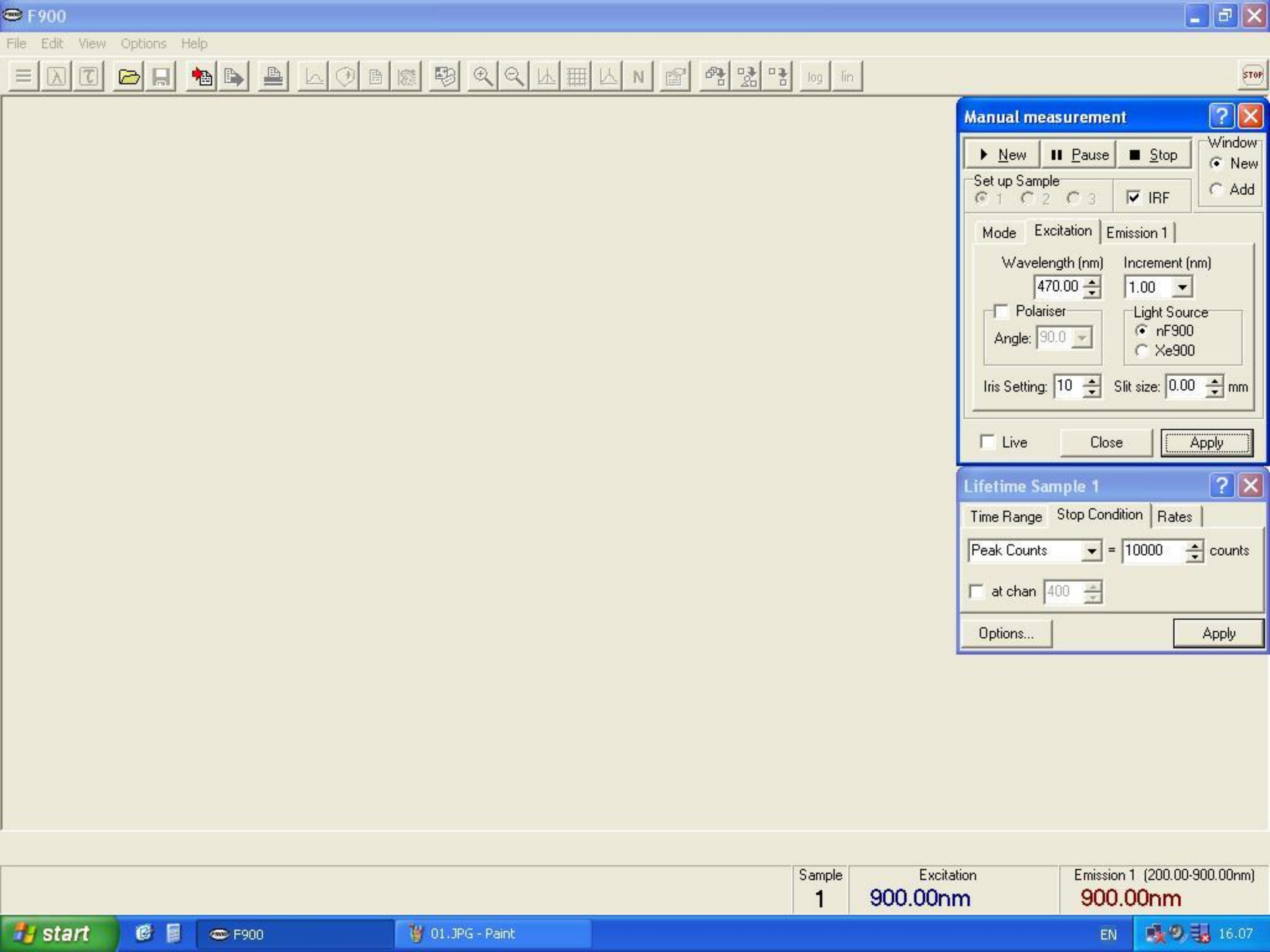


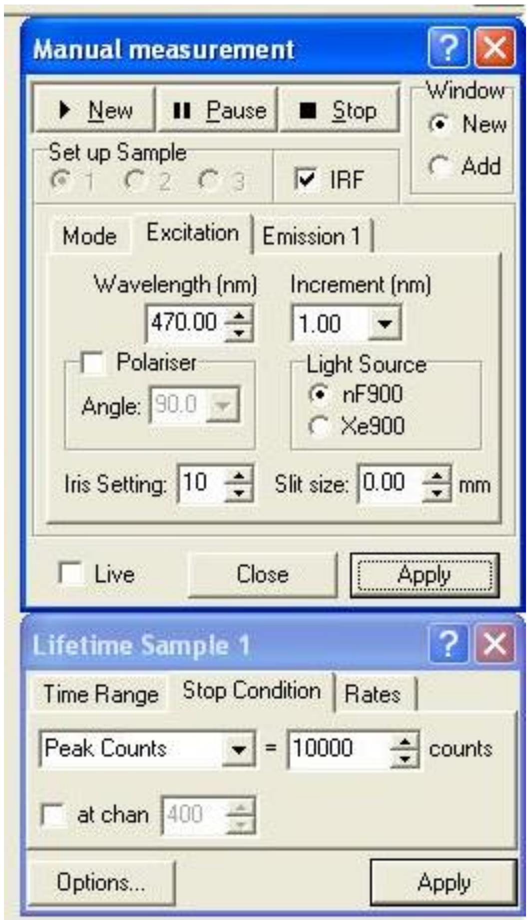


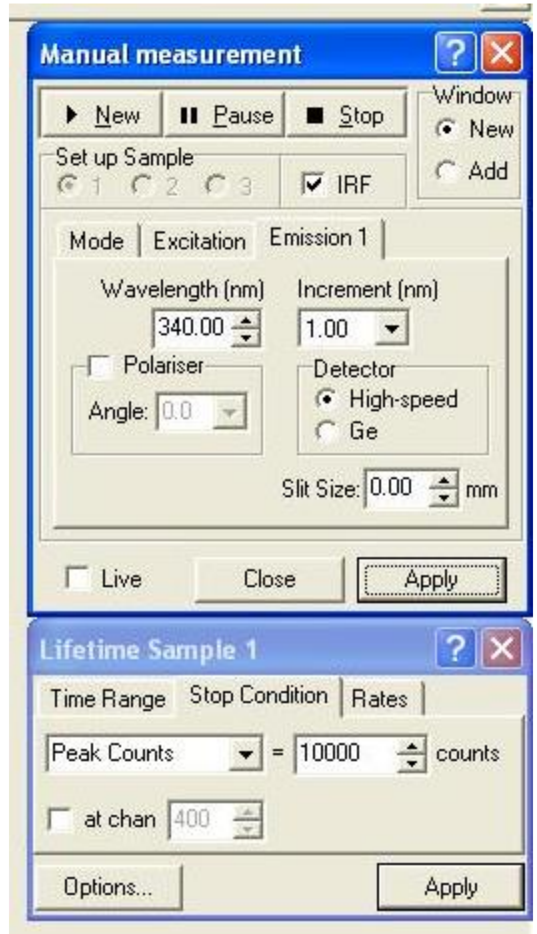

PDL 800-B
PULSED DIODE LASER
REP. FREQUENCY
LASER
TRIGGER
INTENSITY
STBY
ON
LEVEL
SOURCE
TGP110 10MHz Pulse Generator

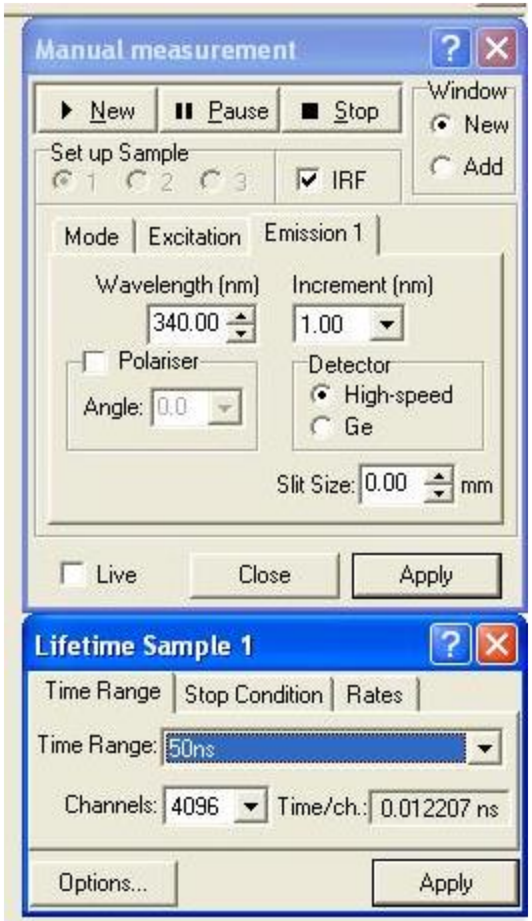

High-speed H5773-04
185-850nm / 22ps
-100mV

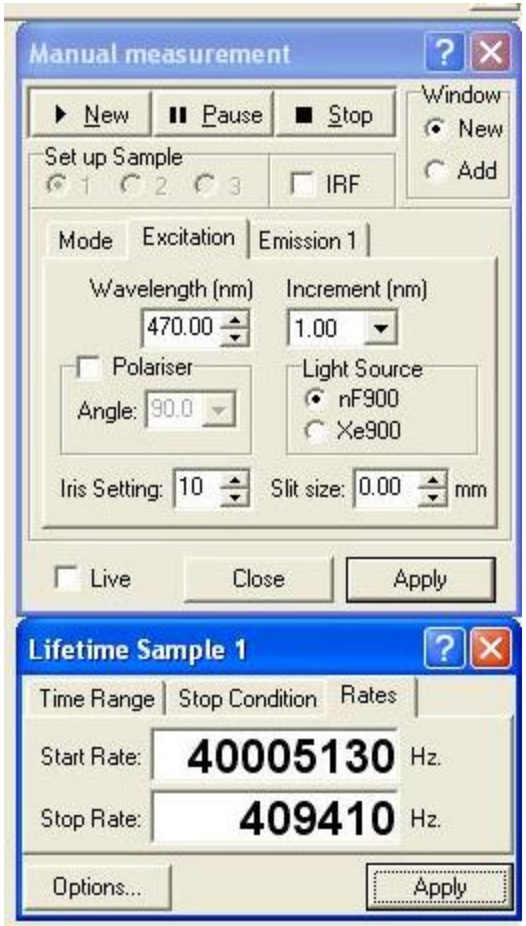

F900
File Edit View Options Help
log lin
Manual Lifetime...
Multiple...
TRES
Anistropy...
Sample
1
Excitation
900.00nm
Emission 1 (200.00-900.00nm)
900.00nm
start
F900
EN
16.06

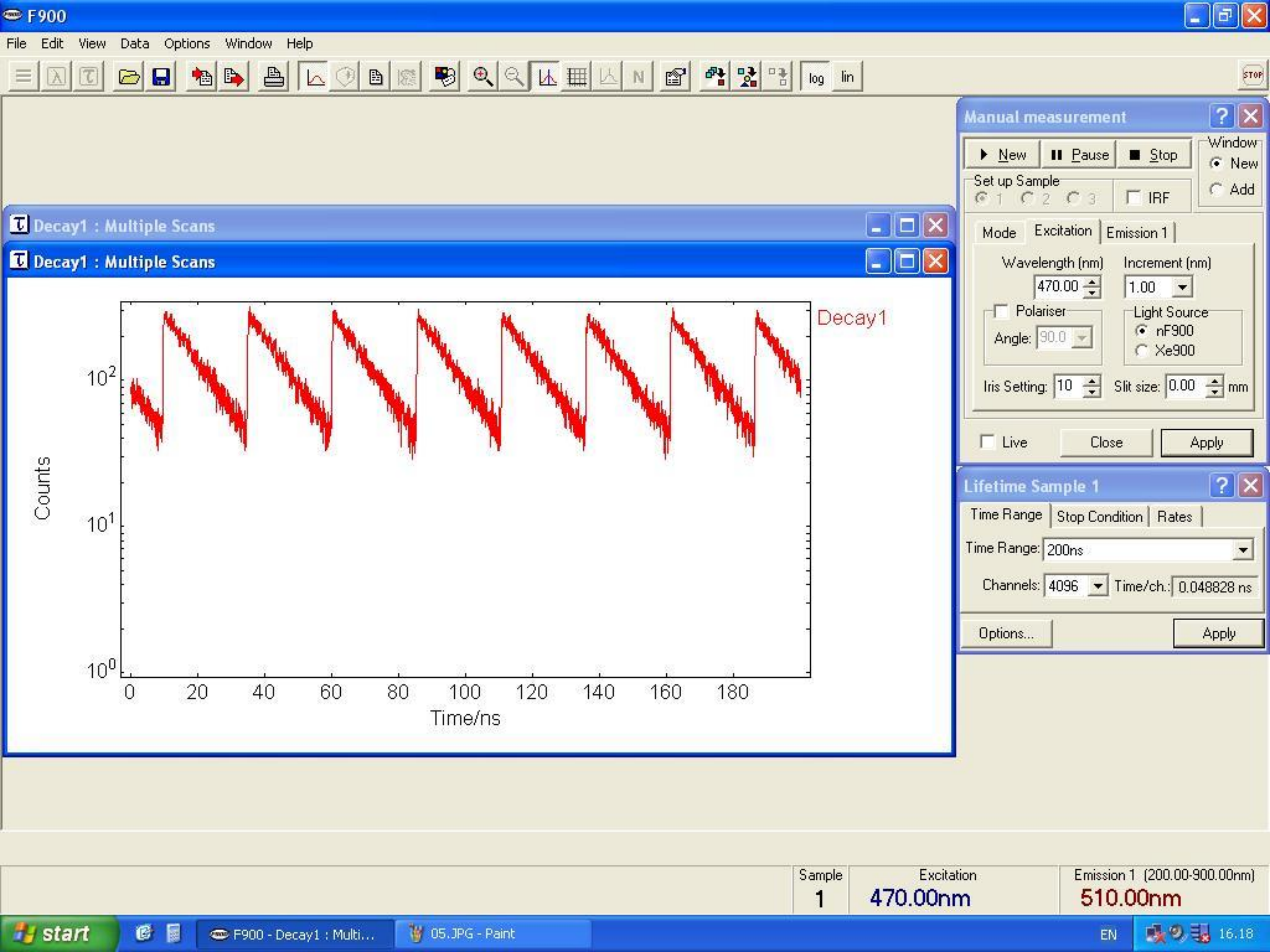

F900
File Edit View Options Help
log lin
STOP
Manual measurement
New Pause Stop
Window
New
Add
Set up Sample
1 2 3
IRF
Mode Excitation Emission 1
Wavelength (nm)
470.00
Increment (nm)
1.00
Polariser
Angle: 90.0
Light Source
nF900
Xe900
Iris Setting: 10
Slit size: 0.00 mm
Live
Close
Apply
Lifetime Sample 1
Time Range Stop Condition Rates
Peak Counts = 10000 counts
at chan 400
Options...
Apply
Sample
1
Excitation
900.00nm
Emission 1 (200.00-900.00nm)
900.00nm
start
F900
01.JPG - Paint
EN
16.07

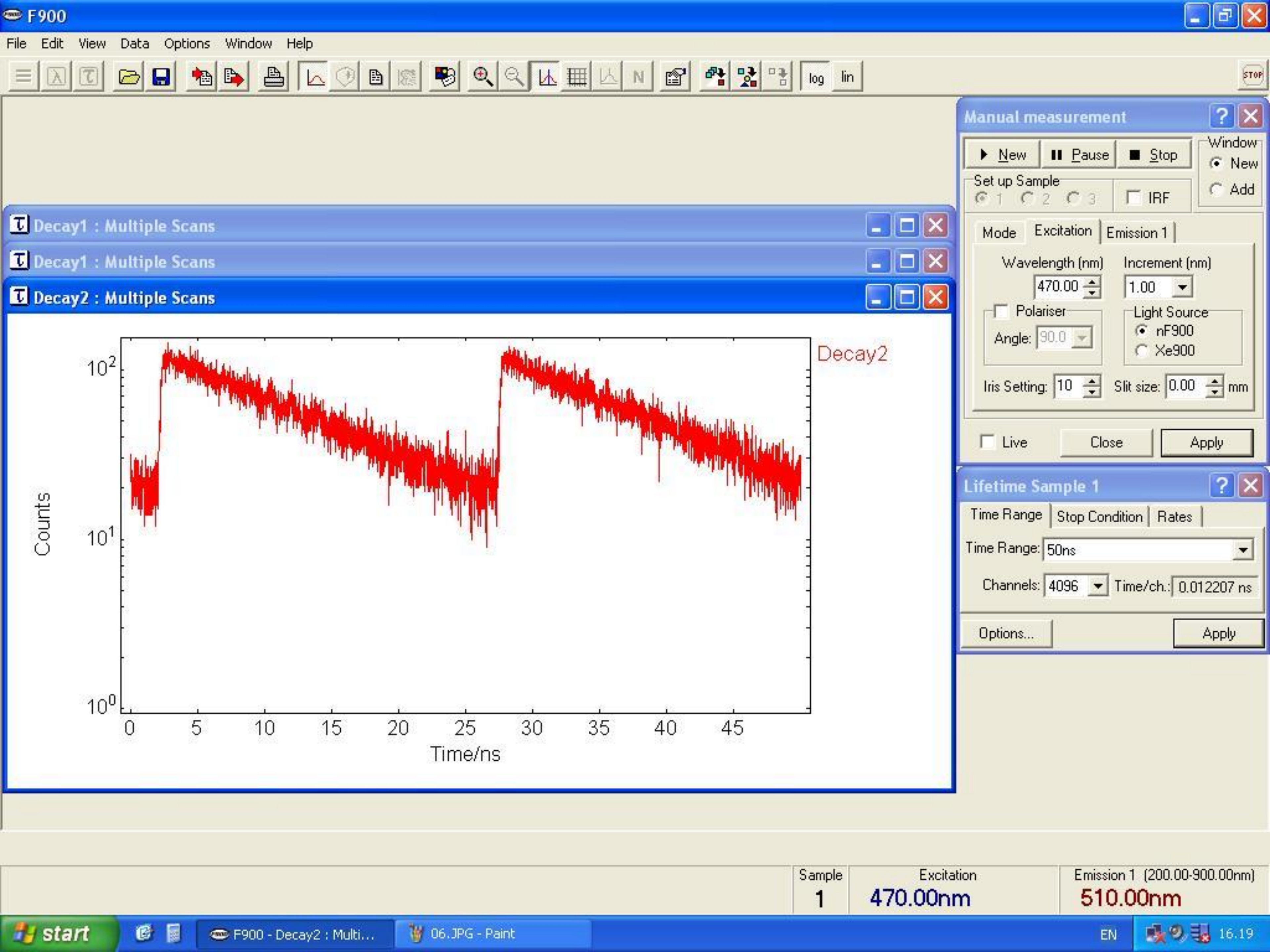

Manual measurement
New
Pause
Stop
Window
New
Add
Set up Sample
1
2
3
IRF
Mode
Excitation
Emission 1
Wavelength (nm)
470.00
Increment (nm)
1.00
Polariser
Angle:
90.0
Light Source
nF900
Xe900
Iris Setting:
10
Slit size:
0.00
mm
Live
Close
Apply
Lifetime Sample 1
Time Range
Stop Condition
Rates
Peak Counts
=
10000
counts
at chan
400
Options...
Apply

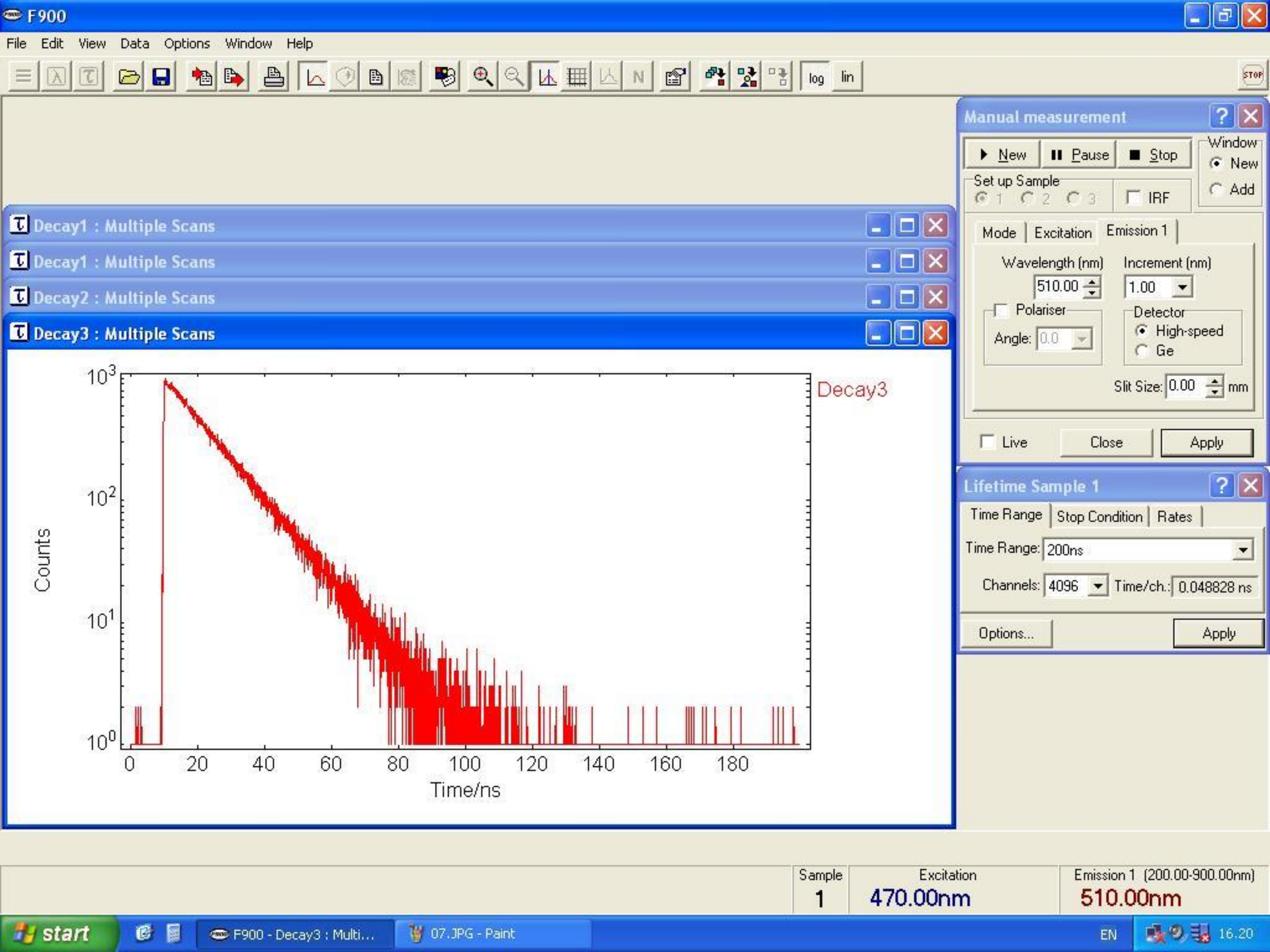

Manual measurement
New
Pause
Stop
Window
New
Add
Set up Sample
1
2
3
IRF
Mode
Excitation
Emission 1
Wavelength (nm)
340.00
Increment (nm)
1.00
Polariser
Angle:
0.0
Detector
High-speed
Ge
Slit Size:
0.00
mm
Live
Close
Apply
Lifetime Sample 1
Time Range
Stop Condition
Rates
Peak Counts
=
10000
counts
at chan
400
Options...
Apply


Manual measurement
New
Pause
Stop
Window
New
Add
Set up Sample
1 2 3
IRF
Mode
Excitation
Emission 1
Wavelength (nm)
340.00
Increment (nm)
1.00
Polariser
Angle: 0.0
Detector
High-speed
Ge
Slit Size: 0.00 mm
Live
Close
Apply
Lifetime Sample 1
Time Range
Stop Condition
Rates
Time Range: 50ns
Channels: 4096
Time/ch.: 0.012207 ns
Options...
Apply

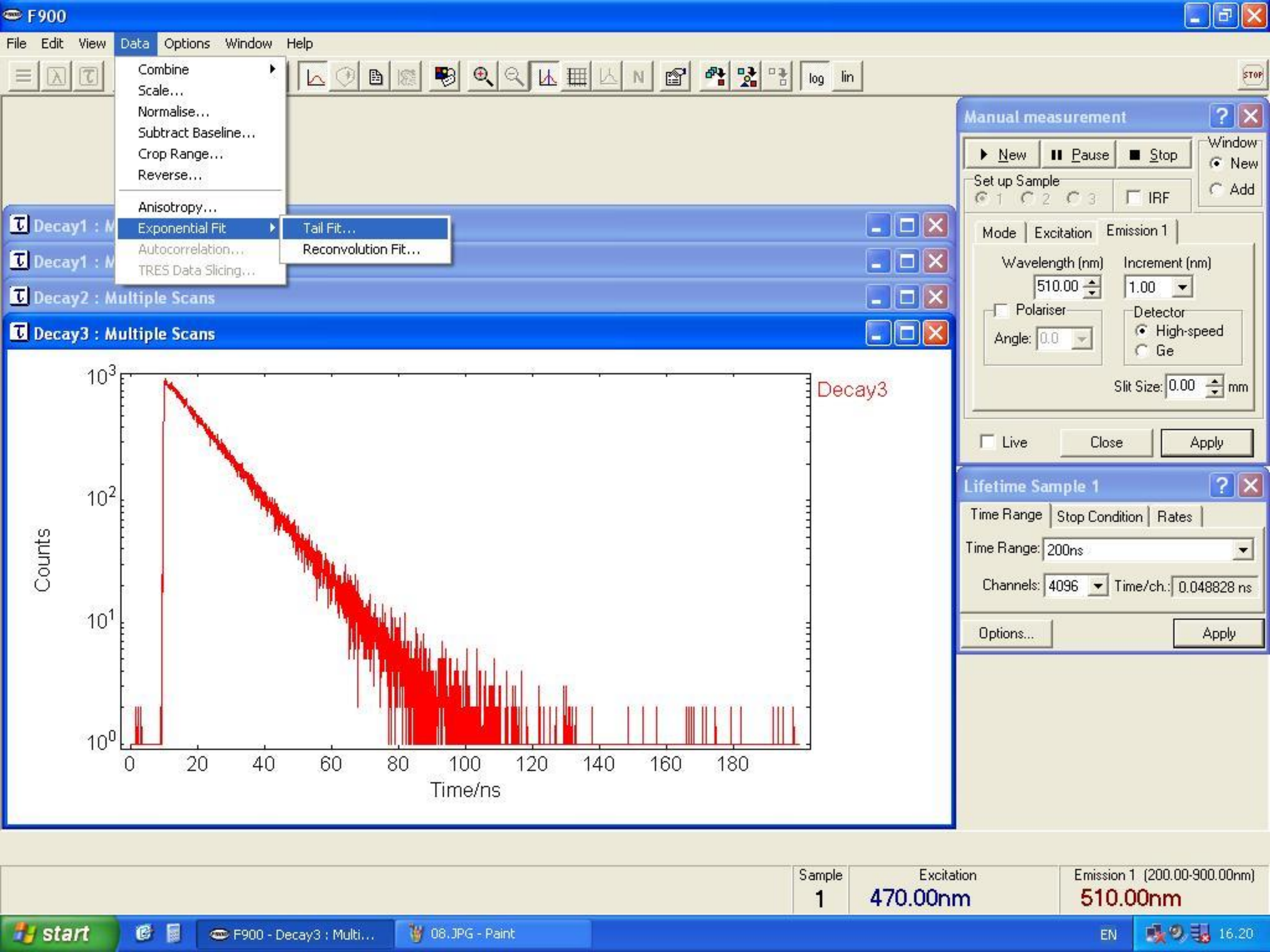

Manual measurement
New
Pause
Stop
Window
New
Add
Set up Sample
1 2 3
IRF
Mode
Excitation
Emission 1
Wavelength (nm)
470.00
Increment (nm)
1.00
Polariser
Angle: 90.0
Light Source
nF900
Xe900
Iris Setting: 10
Slit size: 0.00 mm
Live
Close
Apply
Lifetime Sample 1
Time Range
Stop Condition
Rates
Start Rate: 40005130 Hz.
Stop Rate: 409410 Hz.
Options...
Apply

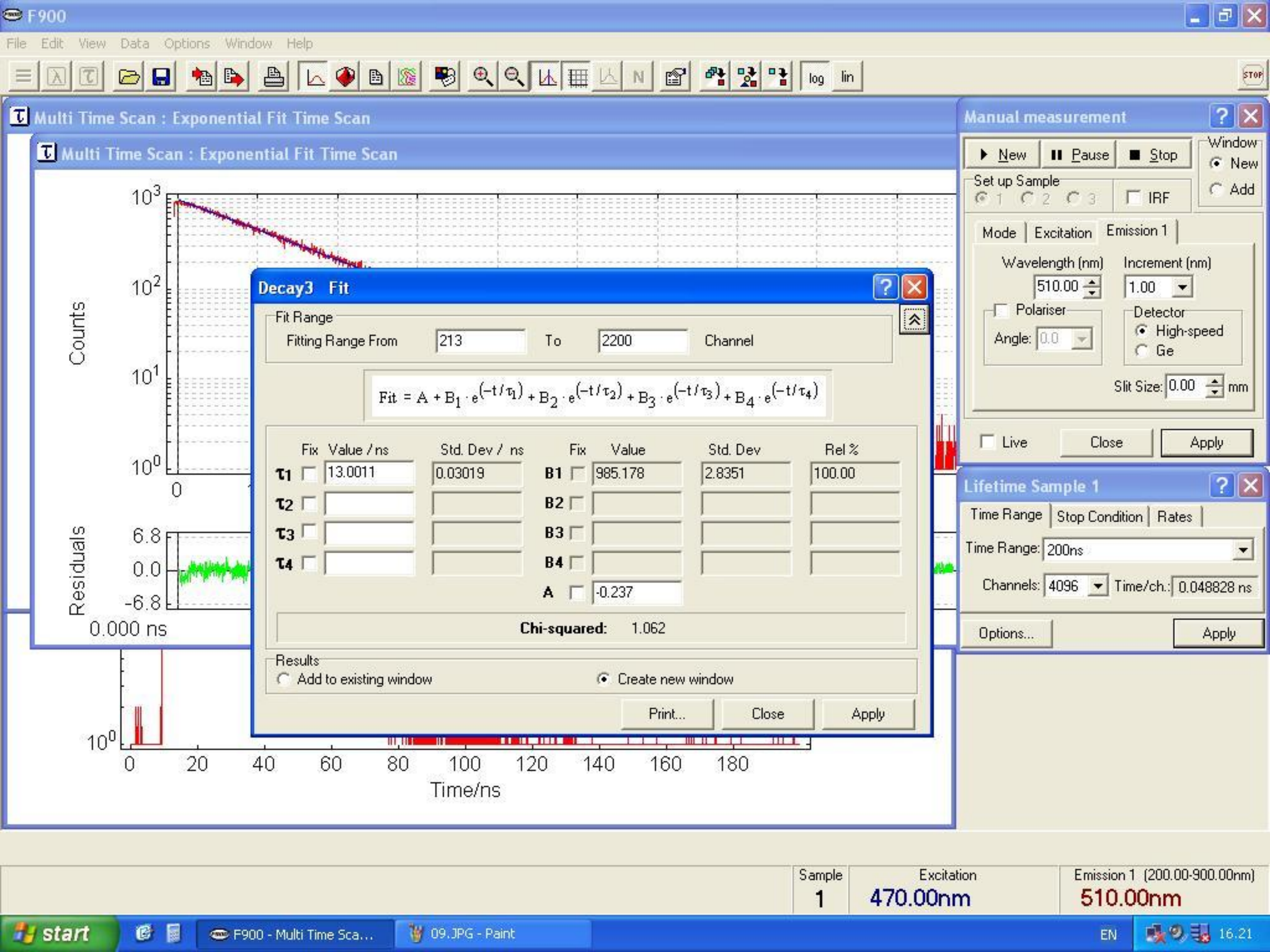

F900
File Edit View Data Options Window Help
log lin
Manual measurement
New Pause Stop
Window
New
Add
Set up Sample
1 2 3
IRF
Mode Excitation Emission 1
Wavelength (nm)
470.00
Increment (nm)
1.00
Polariser
Angle: 90.0
Light Source
nF900
Xe900
Iris Setting: 10
Slit size: 0.00 mm
Live
Close
Apply
Lifetime Sample 1
Time Range Stop Condition Rates
Time Range: 200ns
Channels: 4096
Time/ch.: 0.048828 ns
Options...
Apply
Decay1 : Multiple Scans
Decay1 : Multiple Scans
Decay1
Counts
10^2
10^1
10^0
0 20 40 60 80 100 120 140 160 180
Time/ns
Sample
1
Excitation
470.00nm
Emission 1 (200.00-900.00nm)
510.00nm
start
F900 - Decay1 : Multi...
05.JPG - Paint
EN
16.18

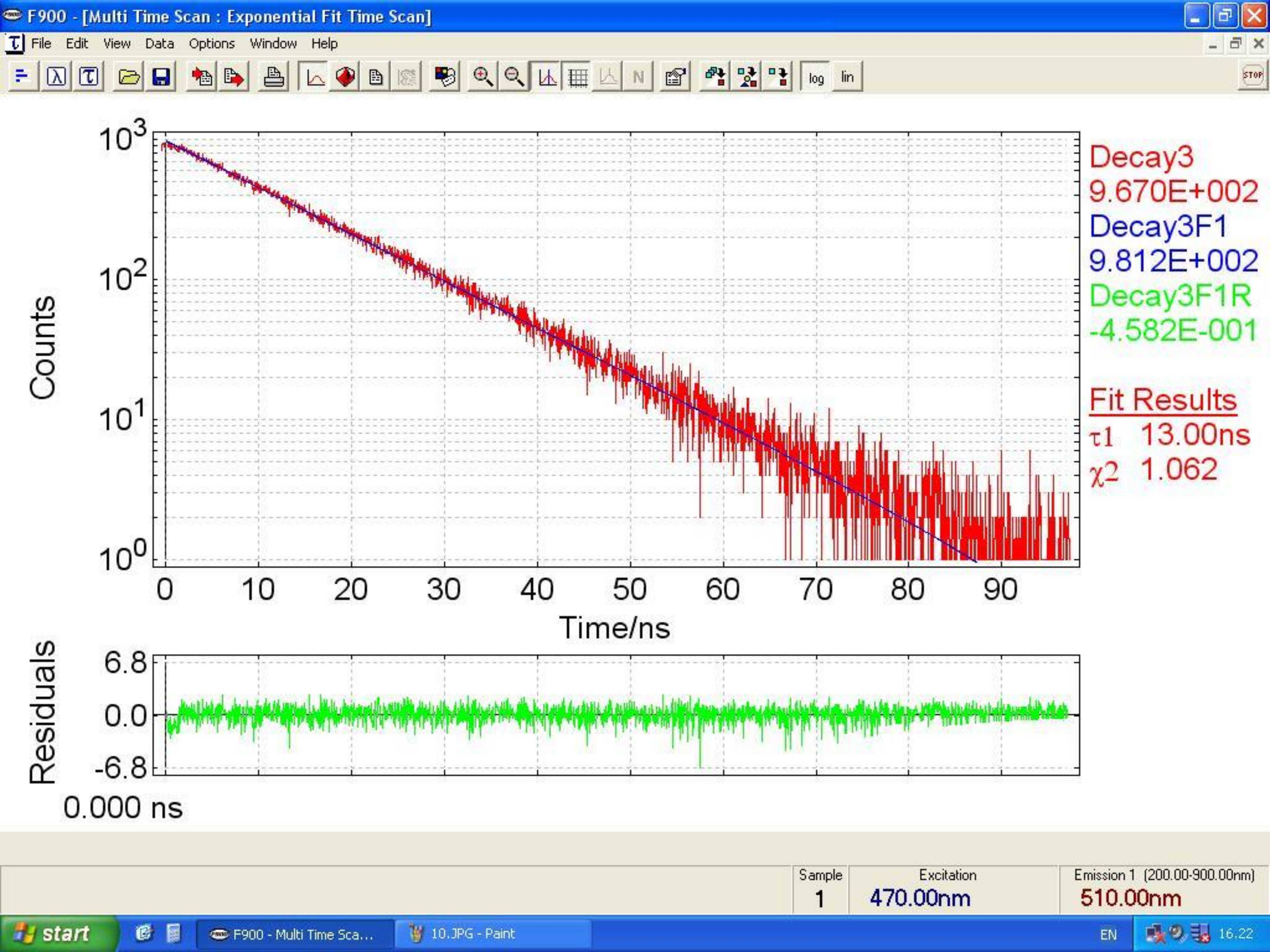

F900
File Edit View Data Options Window Help
log lin
Decay1 : Multiple Scans
Decay1 : Multiple Scans
Decay2 : Multiple Scans
Decay2
Counts
Time/ns
Manual measurement
New Pause Stop
Window
New
Add
Set up Sample
IRF
Mode Excitation Emission 1
Wavelength (nm) Increment (nm)
470.00 1.00
Polariser
Angle: 90.0
Light Source
nF900
Xe900
Iris Setting: 10 Slit size: 0.00 mm
Live Close Apply
Lifetime Sample 1
Time Range Stop Condition Rates
Time Range: 50ns
Channels: 4096 Time/ch.: 0.012207 ns
Options... Apply
Sample 1
Excitation 470.00nm
Emission 1 (200.00-900.00nm) 510.00nm
start
F900 - Decay2 : Multi...
06.JPG - Paint
EN 16.19

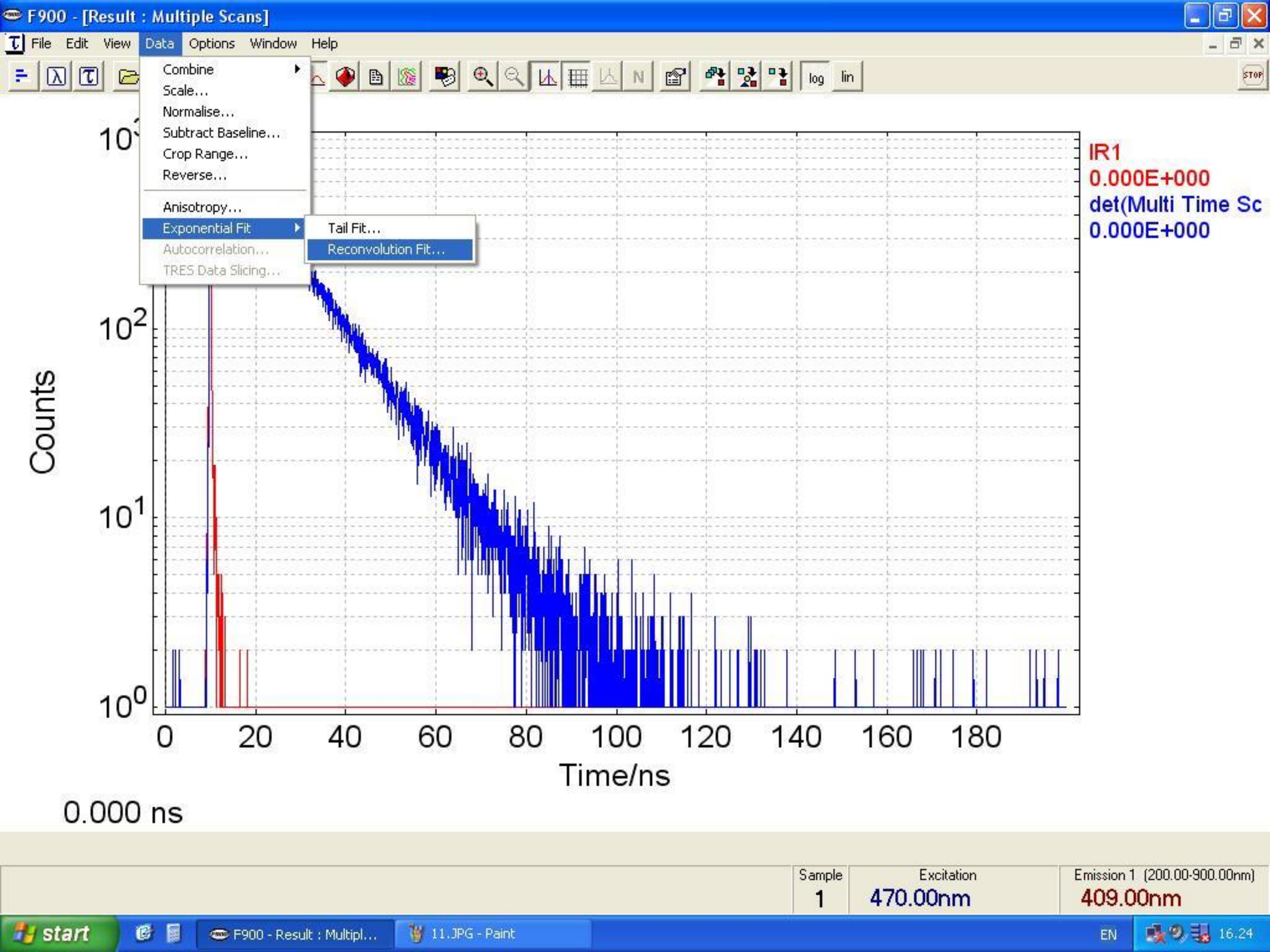


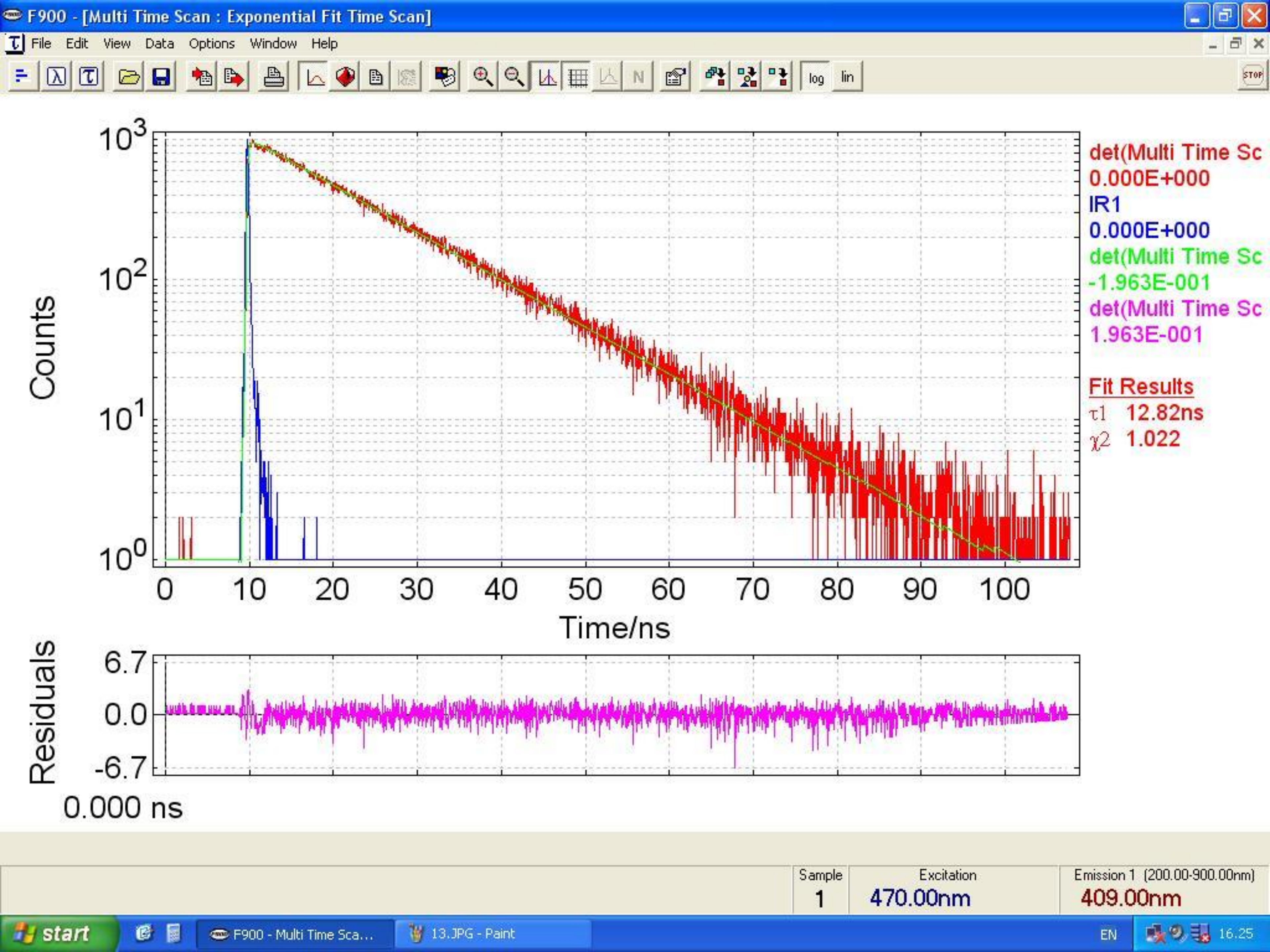
F900
File Edit View Data Options Window Help
log lin
Manual measurement
New Pause Stop
Window
New
Add
Set up Sample
1 2 3
IRF
Mode Excitation Emission 1
Wavelength (nm)
510.00
Increment (nm)
1.00
Polariser
Angle: 0.0
Detector
High-speed
Ge
Slit Size: 0.00 mm
Live Close Apply
Lifetime Sample 1
Time Range Stop Condition Rates
Time Range: 200ns
Channels: 4096 Time/ch.: 0.048828 ns
Options... Apply
Decay1 : Multiple Scans
Decay1 : Multiple Scans
Decay2 : Multiple Scans
Decay3 : Multiple Scans
Decay3
Counts
Time/ns
Sample
1
Excitation
470.00nm
Emission 1 (200.00-900.00nm)
510.00nm
start
F900 - Decay3 : Multi...
07.JPG - Paint
EN
16.20


F900
File Edit View Data Options Window Help
Combine
Scale...
Normalise...
Subtract Baseline...
Crop Range...
Reverse...
Anisotropy...
Exponential Fit
Tail Fit...
Reconvolution Fit...
Autocorrelation...
TRES Data Slicing...
log lin
Decay2 : Multiple Scans
Decay3 : Multiple Scans
Decay3
Counts
Time/ns
Manual measurement
New Pause Stop
Window
New
Add
Set up Sample
IRF
Mode Excitation Emission 1
Wavelength (nm)
Increment (nm)
510.00
1.00
Polariser
Angle: 0.0
Detector
High-speed
Ge
Slit Size: 0.00 mm
Live Close Apply
Lifetime Sample 1
Time Range Stop Condition Rates
Time Range: 200ns
Channels: 4096 Time/ch.: 0.048828 ns
Options... Apply
Sample
1
Excitation
470.00nm
Emission 1 (200.00-900.00nm)
510.00nm
start
F900 - Decay3 : Multi...
08.JPG - Paint
EN 16.20


F900
File Edit View Data Options Window Help
Multi Time Scan : Exponential Fit Time Scan
Counts
Residuals
0.000 ns
Time/ns
Decay3 Fit
Fit Range
Fitting Range From 213 To 2200 Channel
$Fit = A + B_1 \cdot e^{(-t/\tau_1)} + B_2 \cdot e^{(-t/\tau_2)} + B_3 \cdot e^{(-t/\tau_3)} + B_4 \cdot e^{(-t/\tau_4)}$
Fix Value / ns Std. Dev / ns Fix Value Std. Dev Rel %
τ1 13.0011 0.03019 B1 985.178 2.8351 100.00
τ2 B2
τ3 B3
τ4 B4
A -0.237
Chi-squared: 1.062
Results
Add to existing window
Create new window
Print... Close Apply
Manual measurement
New Pause Stop
Window New Add
Set up Sample 1 2 3 IRF
Mode Excitation Emission 1
Wavelength (nm) 510.00
Increment (nm) 1.00
Polariser
Angle: 0.0
Detector High-speed Ge
Slit Size: 0.00 mm
Live Close Apply
Lifetime Sample 1
Time Range Stop Condition Rates
Time Range: 200ns
Channels: 4096 Time/ch.: 0.048828 ns
Options... Apply
Sample 1
Excitation 470.00nm
Emission 1 (200.00-900.00nm) 510.00nm
start F900 - Multi Time Sca... 09.JPG - Paint EN 16.21


F900 - [Multi Time Scan : Exponential Fit Time Scan]
File Edit View Data Options Window Help
log lin
Counts
Time/ns
Residuals
0.000 ns
Decay3
9.670E+002
Decay3F1
9.812E+002
Decay3F1R
-4.582E-001
Fit Results
τ1 13.00ns
χ2 1.062
Sample
1
Excitation
470.00nm
Emission 1 (200.00-900.00nm)
510.00nm
start
F900 - Multi Time Sca...
10.JPG - Paint
EN
16.22


F900 - [Result : Multiple Scans]
File Edit View Data Options Window Help
Combine
Scale...
Normalise...
Subtract Baseline...
Crop Range...
Reverse...
Anisotropy...
Exponential Fit
Autocorrelation...
TRES Data Slicing...
Tail Fit...
Reconvolution Fit...
log
lin
STOP
IR1
0.000E+000
det(Multi Time Sc
0.000E+000
Counts
10^2
10^1
10^0
0
20
40
60
80
100
120
140
160
180
Time/ns
0.000 ns
Sample
1
Excitation
470.00nm
Emission 1 (200.00-900.00nm)
409.00nm
start
F900 - Result : Multipl...
11.JPG - Paint
EN
16.24


F900 - [Multi Time Scan : Exponential Fit Time Scan]
File Edit View Data Options Window Help
log lin
STOP
Counts
10^3
10^2
10^1
10^0
0 10 20 30 40 50 60 70 80 90 100
Time/ns
Residuals
6.7
0.0
-6.7
0.000 ns
det(Multi Time Sc
0.000E+000
IR1
0.000E+000
det(Multi Time Sc
-1.963E-001
det(Multi Time Sc
1.963E-001
Fit Results
τ1 12.82ns
χ2 1.022
Sample
1
Excitation
470.00nm
Emission 1 (200.00-900.00nm)
409.00nm
start
F900 - Multi Time Sca...
13.JPG - Paint
EN
16.25