5. Inorganic semiconductors

5.3 Advanced optical experimental methods to characterize inorganic semiconductors

Topics of this lecture:

- Time-correlated single photon counting: Measure time-resolved fluorescence
- Transient absorption: Measure time-resolved changes in absorption

Fluorescence Lifetimes

Time-Correlated Single Photon Counting (TCSPC)

Timescales

- Reminder: Natural lifetime τ_f can be calculated from measured lifetime τ and QY:

$$\tau_f = \frac{\tau}{\mathbf{\Phi}_f}$$

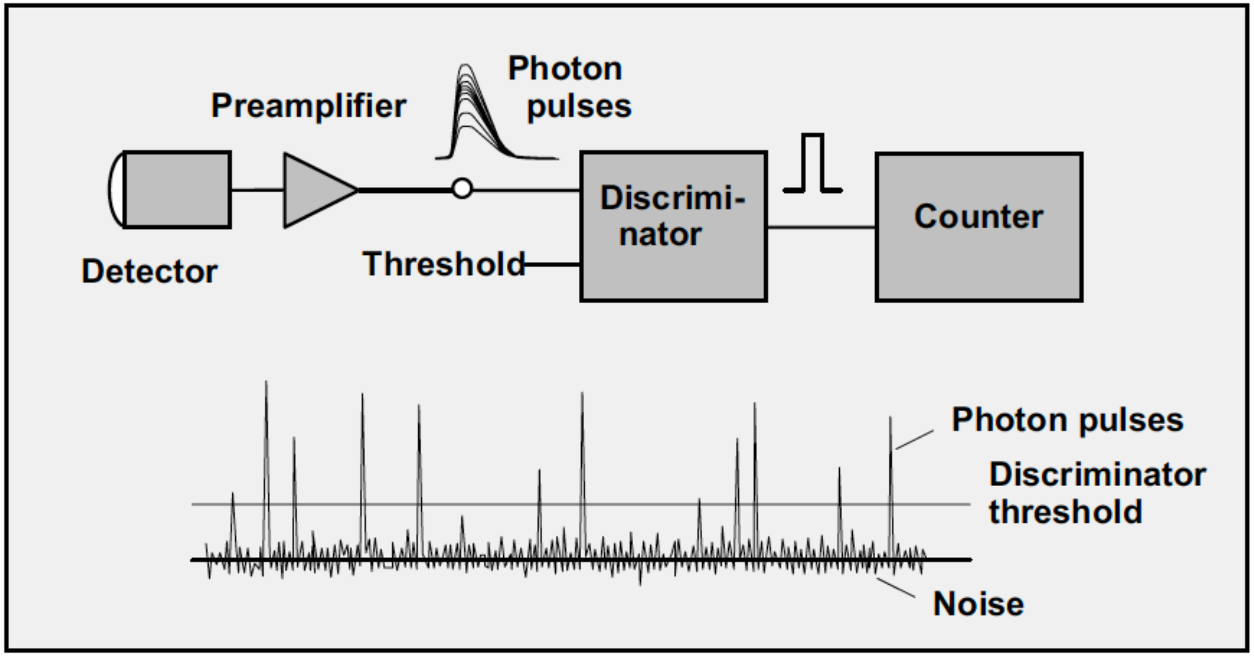
- *We saw how to obtain $\mathbf{\Phi}_f$ - But how do we measure τ of fluorescence/phosphorescence?*

Process	Timescale
Absorption	10^{-16} s (sub-femtosecond)
Vibrational relaxation	10^{-12} s (picosecond)
Internal conversion	10^{-9} -10^{-6} s (nano-microsecond)
Fluorescence	10^{-9} (nanosecond)
Intersystem crossing	10^{-9} -10^{-6} s (nano-microsecond)
Phosphorescence	Seconds-hours (forbidden transition)

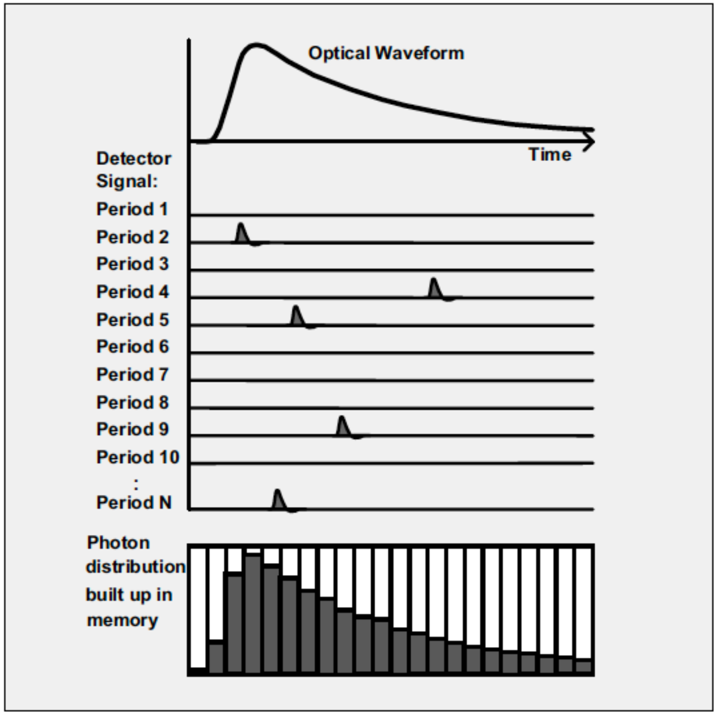
Photo luminescence

Counting photons

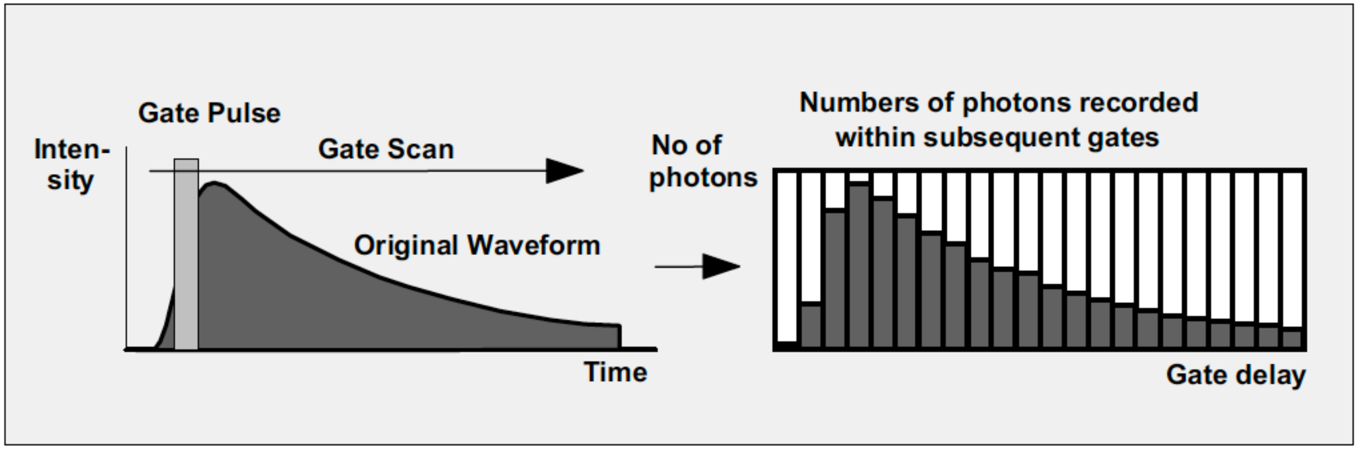
TCSPC allows to see luminescence signals of very low intensity



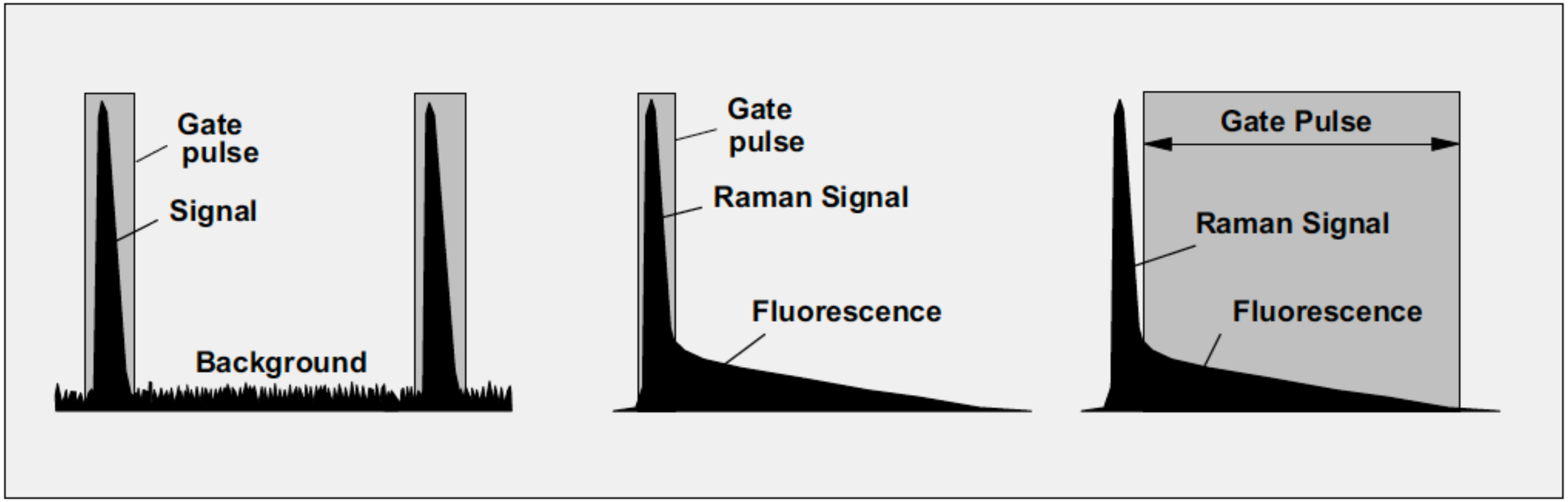
Counting photons “in time”



- Light intensity is so low that the probability of detecting one photon in one signal period (= one laser excitation event) is << 1
- Record the photons, measure their time in the signal period
- Build up a histogram of the photon times



Using the time domain to select a signal

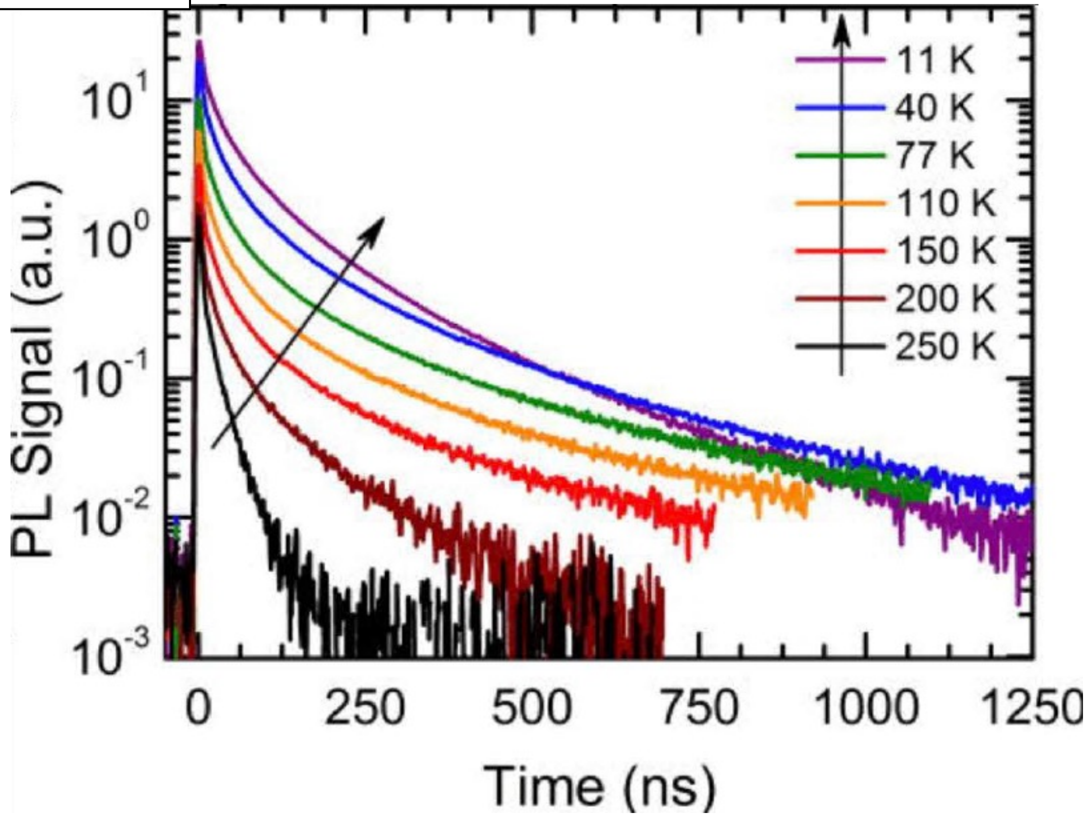


To measure lifetimes…

… you may need to cool down your sample (a lot!)

Example: InAs/$Ga_{1-x}In_xSb$ type-II superlattices (application for IR detectors)
Not a lot of photons at RT! Loss through non-radiative processes
→ Measurement in a cryostat at liquid N_2 or He temperatures are needed!

Excitation 2 µm (0.62 eV)
Detection > 3.6 µm



Steenbergen et al. Appl. Phys. Lett. **99**, 251110 (2011)

Excited-state absorption

Transient Absorption

Modulation techniques

- Perturbing a system in controlled and reproducible manner is one of the most effective ways to investigate it
- The common point to all such techniques is to induce small changes in the sample properties that are measured by using a differential detection
- The time regime of the modulation can vary from impulsive (fast modulation) to quasi steady-state (very slow modulation)

EXAMPLES:

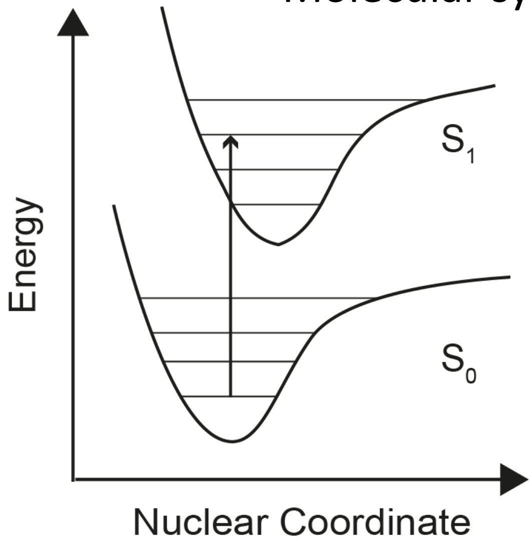
- Electroabsorption: Measure changes in absorption as a function of the applied electric field
- Transient absorption: Measure changes in absorption as a function of time

Excited states

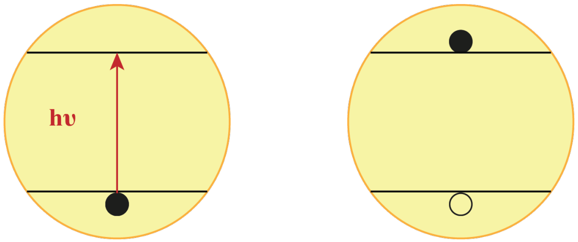
What if we want to look at the **excited state** of molecules or materials?
….There are a lot of things that can happen in the excited state:

Energy transfer, charge transfer, charge trapping…

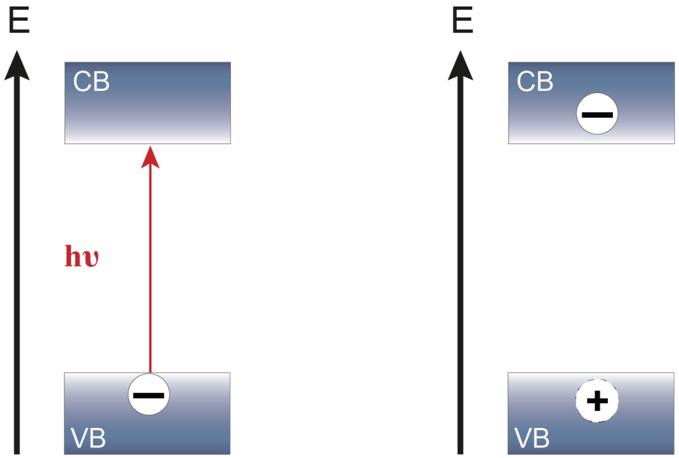
Molecular systems



Nanocrystalline semiconductors



Semiconductors



Can’t we simply photoexcite a sample and measure it?

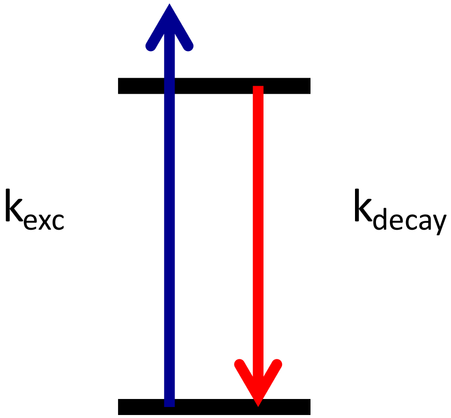
- Photoinduced techniques probe the excited state population at its equilibrium under certain excitation conditions
- Require sufficient build-up of excited state

How to build up enough excited state?

Ideally:

$k_{exc} >> k_{decay}$

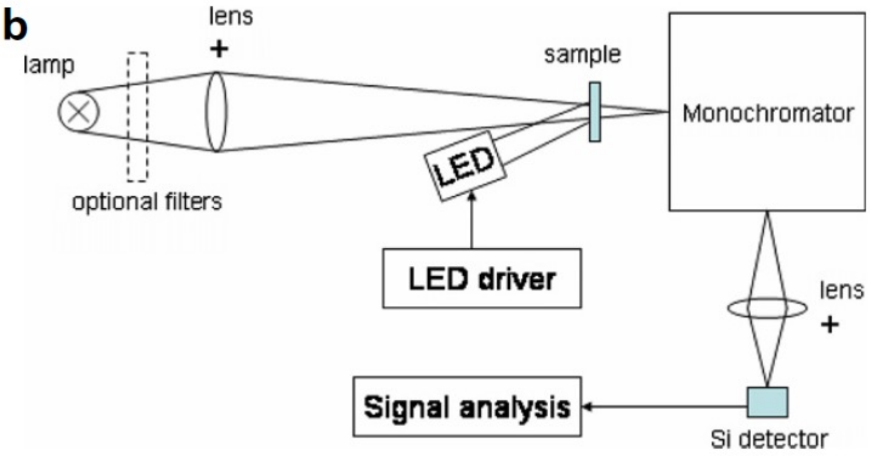
Increase the photons absorbed/s
= more power!
A normal lamp/LED may not be strong enough.
We may need lasers!



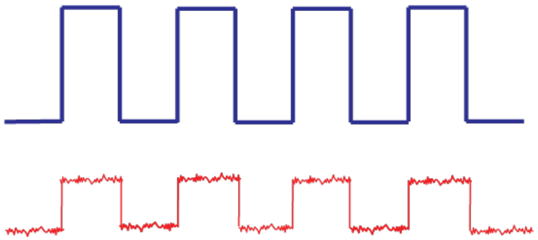
Increase lifetime of the excited state (not always possible)

Measure absorption of excited states

- Photoinduced absorption (PIA)
- Photoexcite the sample with a continuous source and probe its absorption
- Because the signal is very small, need for a lock-in amplifier
- Lock-in amplifier: device that allows to ”lock” at a specific frequency, increases greatly the sensitivity
- PIA gives and idea of the dynamics but it is not straightforward (information encoded in the phase of the signal)



Boschloo, Hagfeldt, *Inorganica Chimica Acta,* **2008**, *361*, 729–734

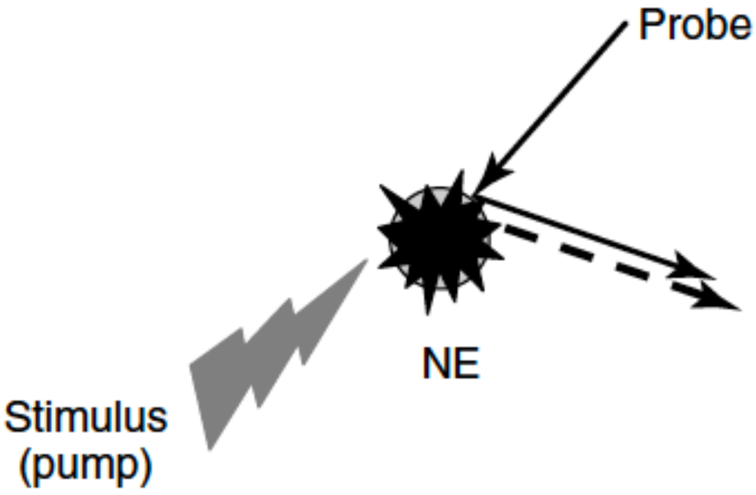


Chopper wheel

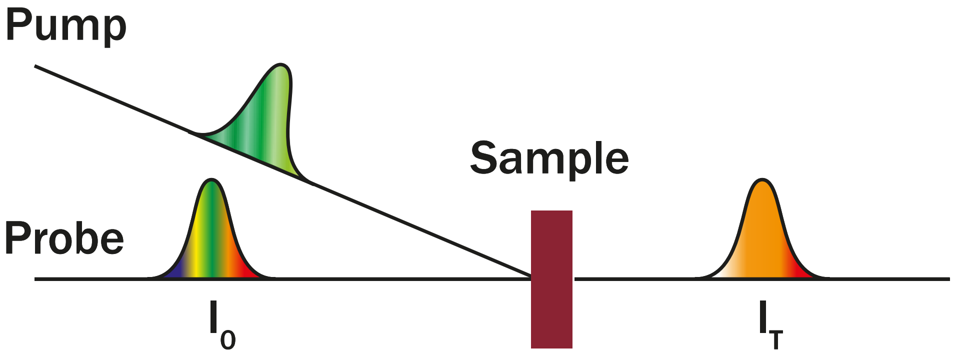
https://www.thorlabs.com/newgrouppage9.cfm?objectgroup_id=287

How to obtain timescales

- A pump probe experiment is the most basic and general approach to time resolution
- A stimulus (**pump**) causes a nonequilibrium state, a **probe** measures this state as it evolves in time



Transient absorption



Pump: Pulsed laser with nanosecond to femtosecond pulses

Probe: A continuous source (lamp) or a pulsed laser

TA measures the change in absorption after pump excitation:

$$\Delta A = A_{pump} - A_{no\ pump}$$

$$\Delta A = -log\left(\frac{I_{T*}}{I_0}\right) + log\left(\frac{I_T}{I_0}\right)$$

$$\boxed{\Delta A = -log\left(\frac{I_{T*}}{I_T}\right)}$$

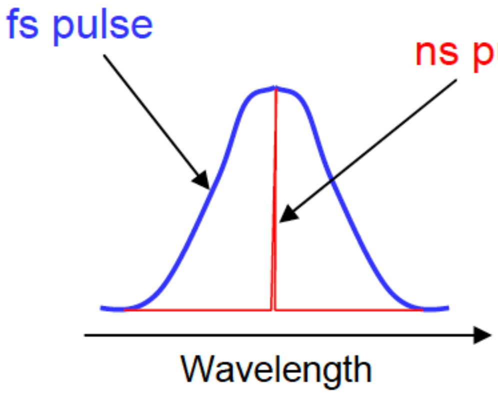
Pulsed lasers vs. continuous lasers

Continous laser	Average Power (W)	Beam radius (cm)	Power/cm^2 (W/cm^2)	
	$1\cdot10^{-3}$	0.2	$8\cdot10^{-3}$	
Pulsed laser	Average Power (W)	Beam radius (cm)	Pulse duration (s)	Peak power/cm^2 per pulse (W/cm^2·pulse)
	$1\cdot10^{-3}$	0.2	$200\cdot10^{-15}$	**$2\cdot10^{5}$**

- **Advantages:** Enormous peak powers will generate enough excited state!

- **Advantage/disadvantage:** Time resolution has to be traded off against energy resolution due to the uncertainty principle:

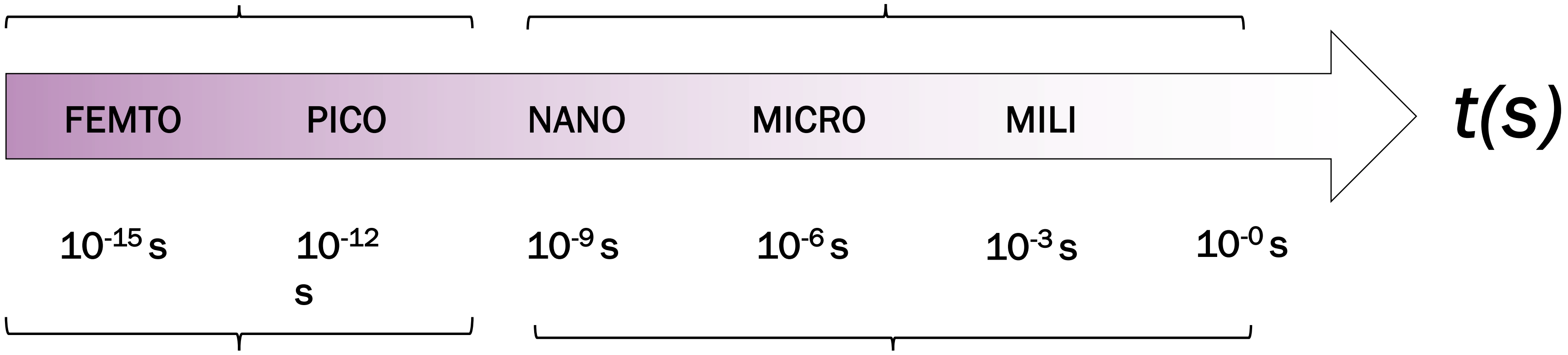
$$\boxed{\Delta E \cdot \Delta t \geq \frac{h}{4\pi}}$$



Timescales

Not possible to use electronics
to resolve
the signal
(except for PL streak camera)

Possible to use
electronics to resolve the
signal



FEMTO PICO NANO MICRO MILI

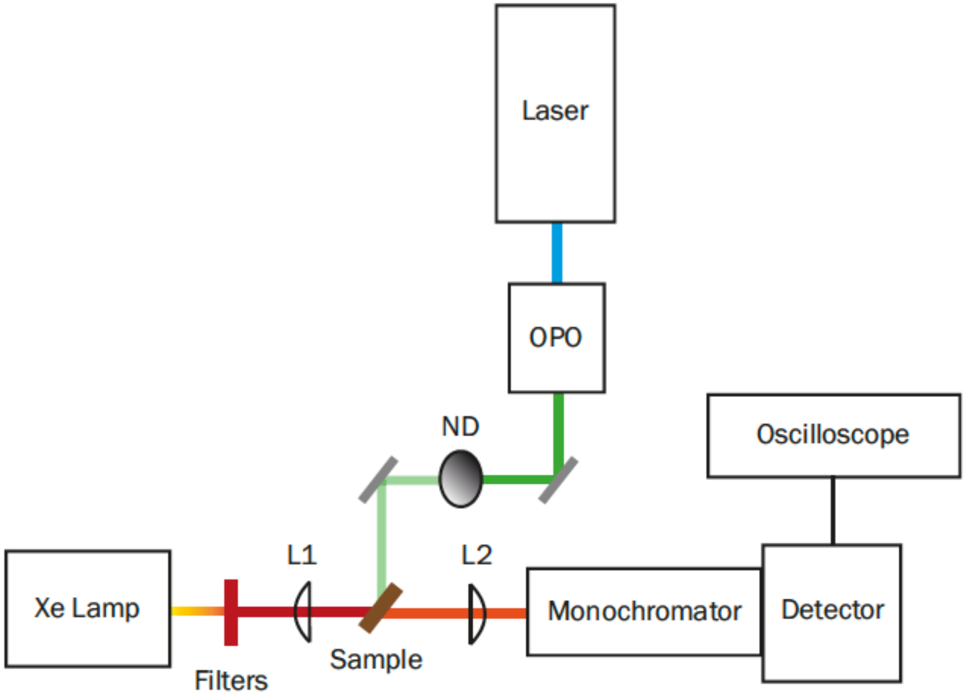
t(s)

10^{-15} s 10^{-12} s 10^{-9} s 10^{-6} s 10^{-3} s 10^{-0} s

Charge transfer
Charge trapping
Vibrational relaxation

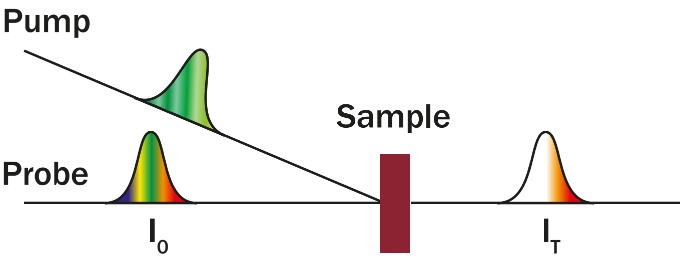
Radiative and non-radiative
recombination

Nanosecond flash photolysis



- The excitation is a short pulse (nanosecond)
- The probe beam is a continuous lamp
- The detection is electronic: We are limited to nanosecond (or picosecond with fancier equipment)
- Difficult to « see electronically » signals $< 10^{-9}$ s
- Below the nanosecond/picosecond: Reconstruct the signal using optical delays!

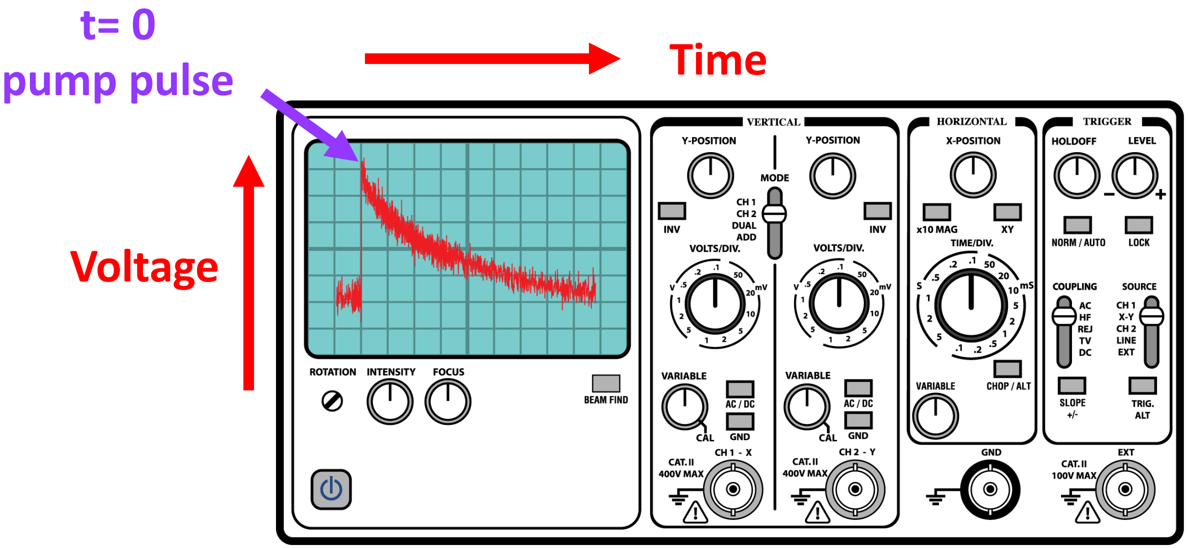
Detection of nanosecond dynamics



Pump: Pulsed laser

Probe: Continous lamp

→ monitor one given wavelength as a function of time with an oscilloscope



- ➢ Difficult to « see » electronically signals below the nanosecond-picosecond
- ➢ Below the nanosecond: reconstruct the time-dependent signal using optical delays!

Detection of subnanosecond dynamics

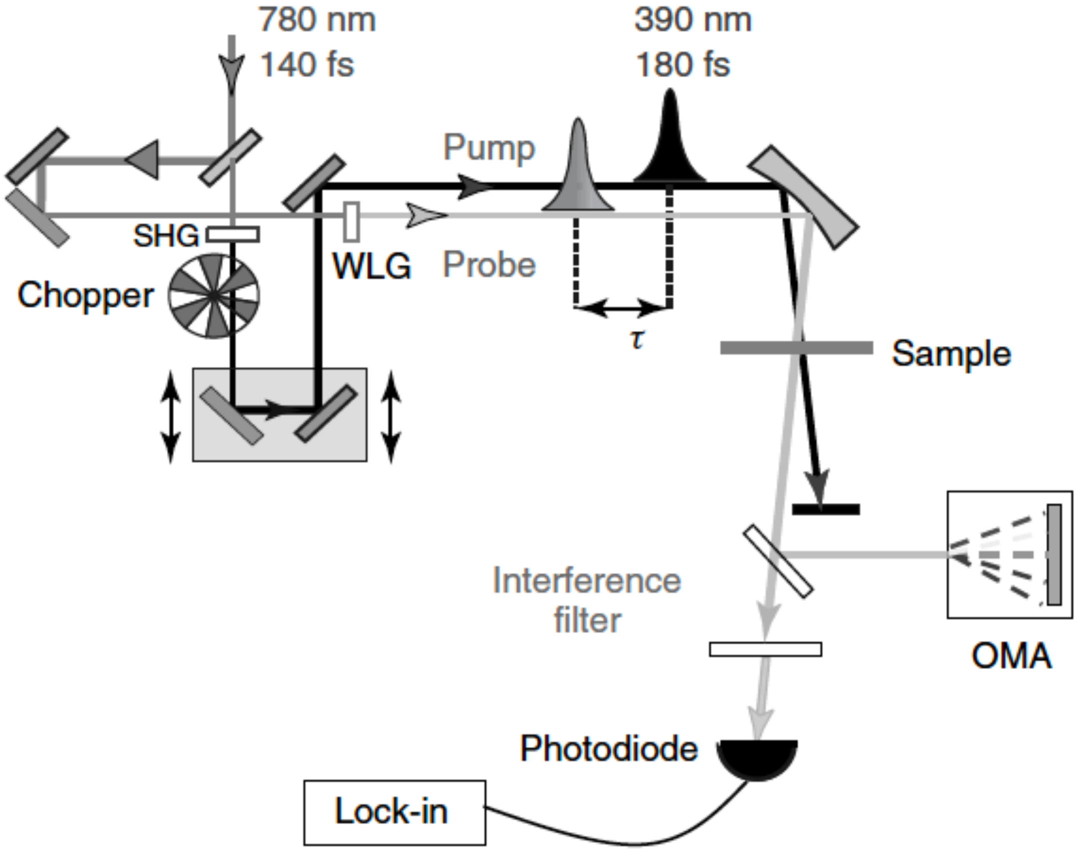
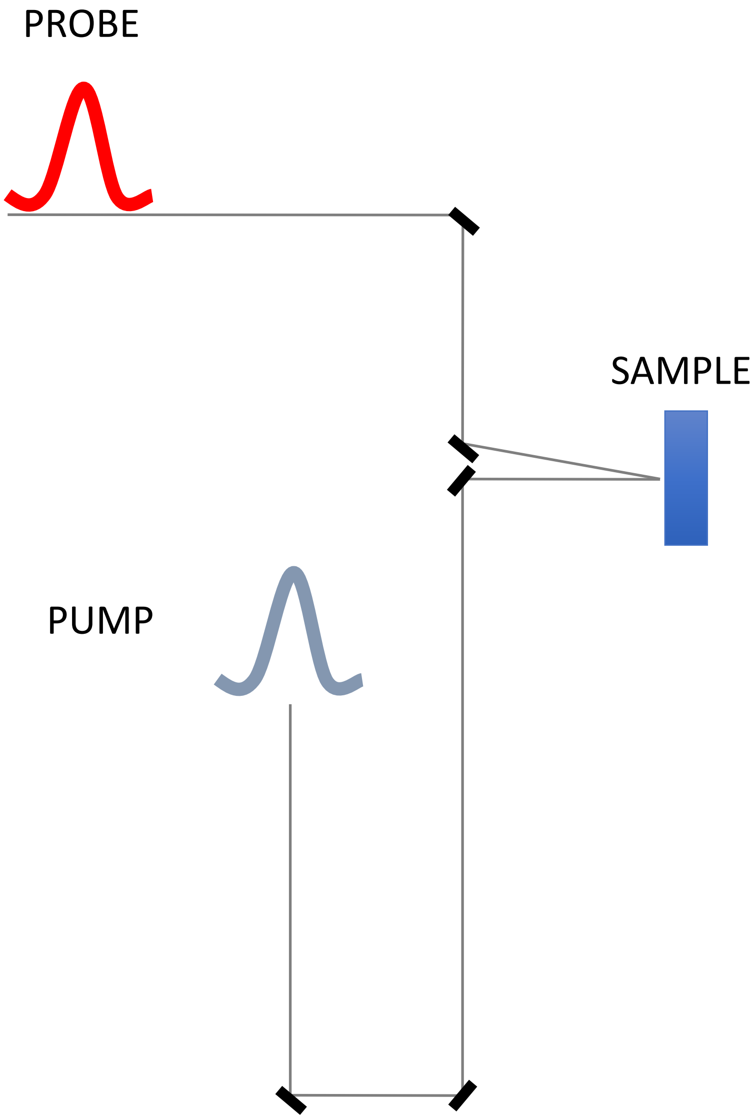
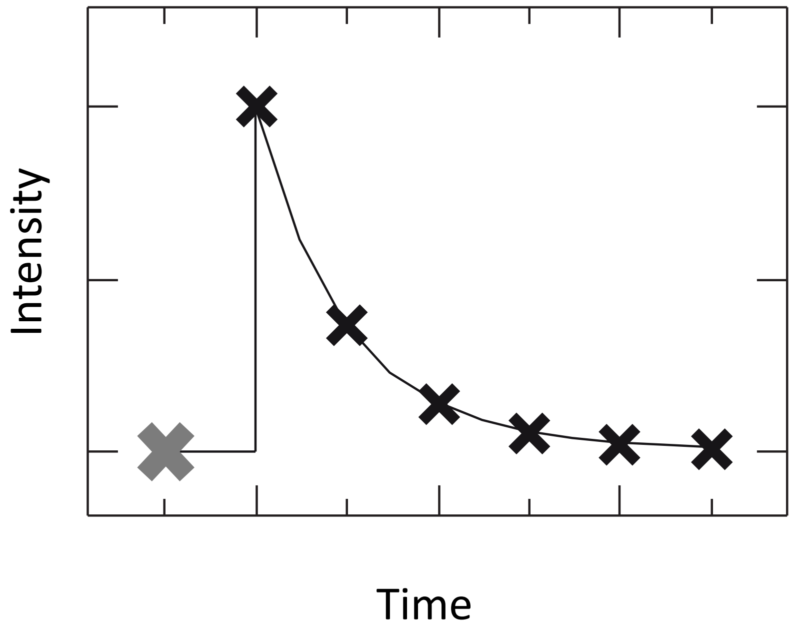


Figure 9.5 A schematic layout of a pump probe setup. SHG, second harmonic generation; WLG, white light generation; OMA, optical multichannel analyzer.

Lanzani, The Photophysics behind Photovoltaics and Photonics

Before excitation

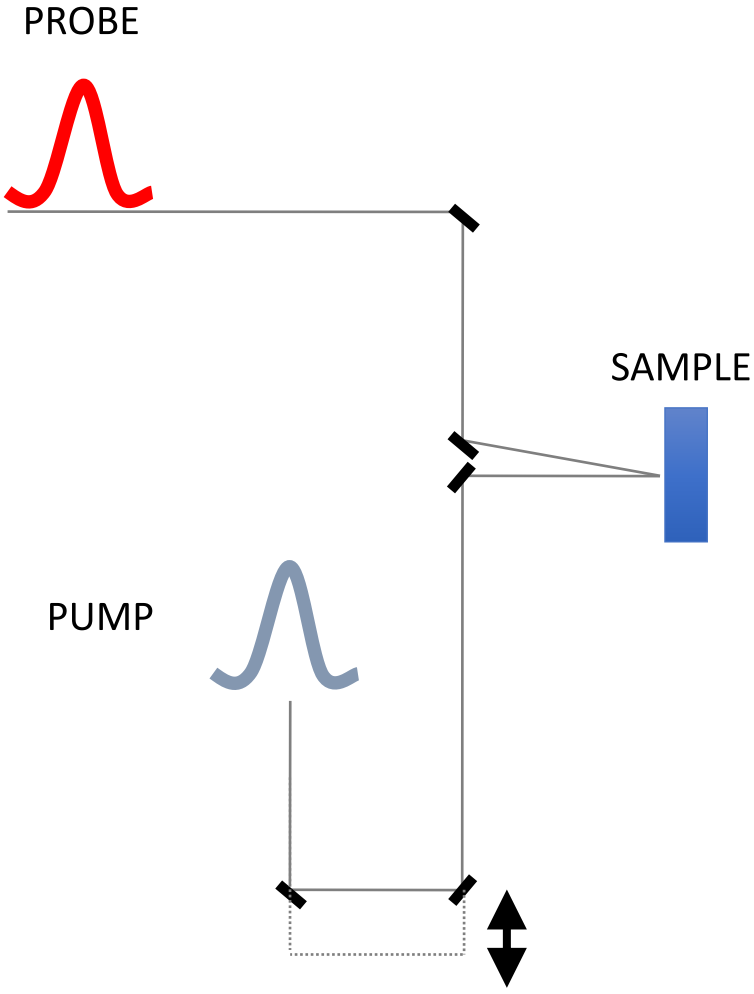




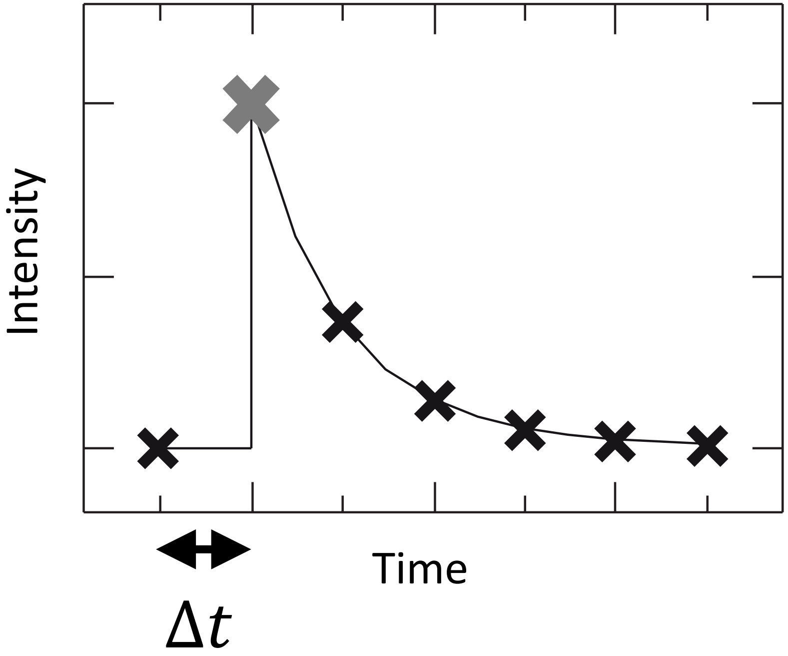
Probe arrives before pump

$\Delta A = 0$ → NO SIGNAL

“Time zero”

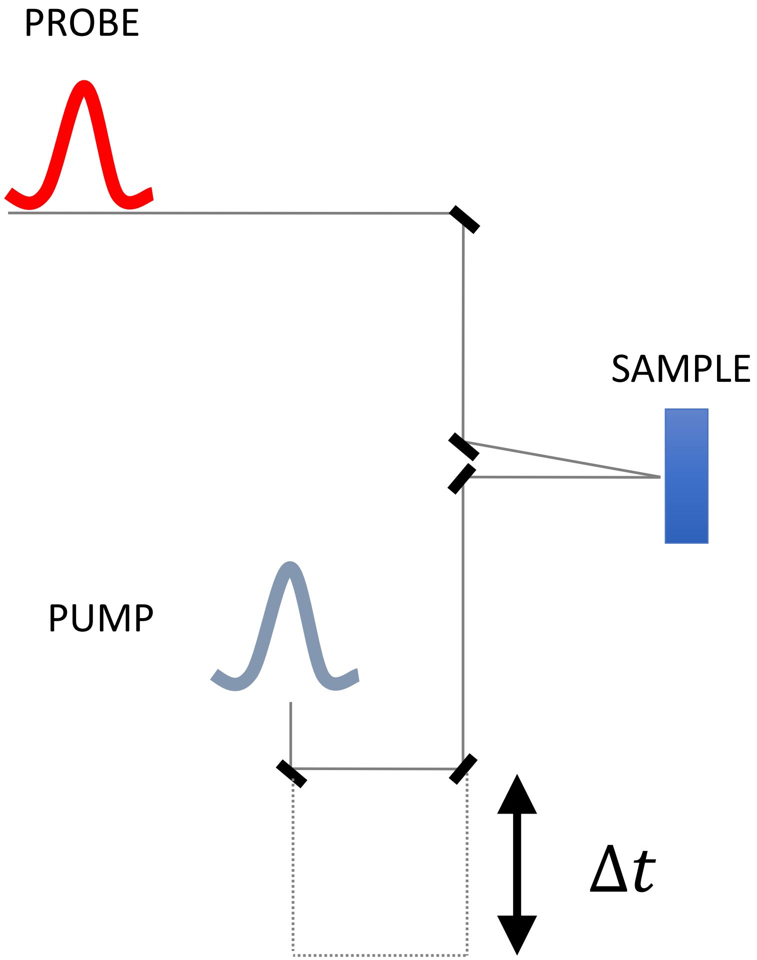


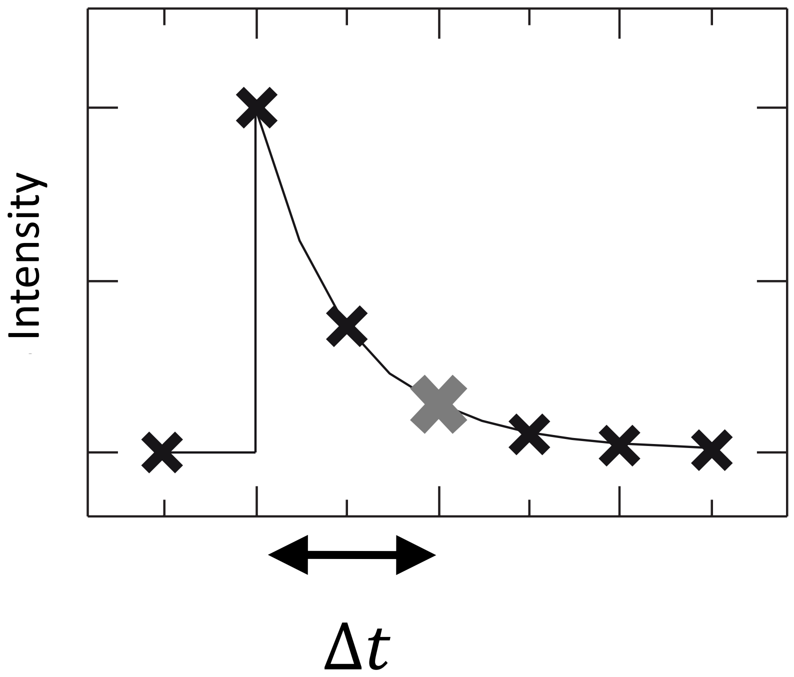
$$\Delta t = \frac{\Delta distance}{speed\ of\ light}$$



The two pulses have travelled the exact same pathlength

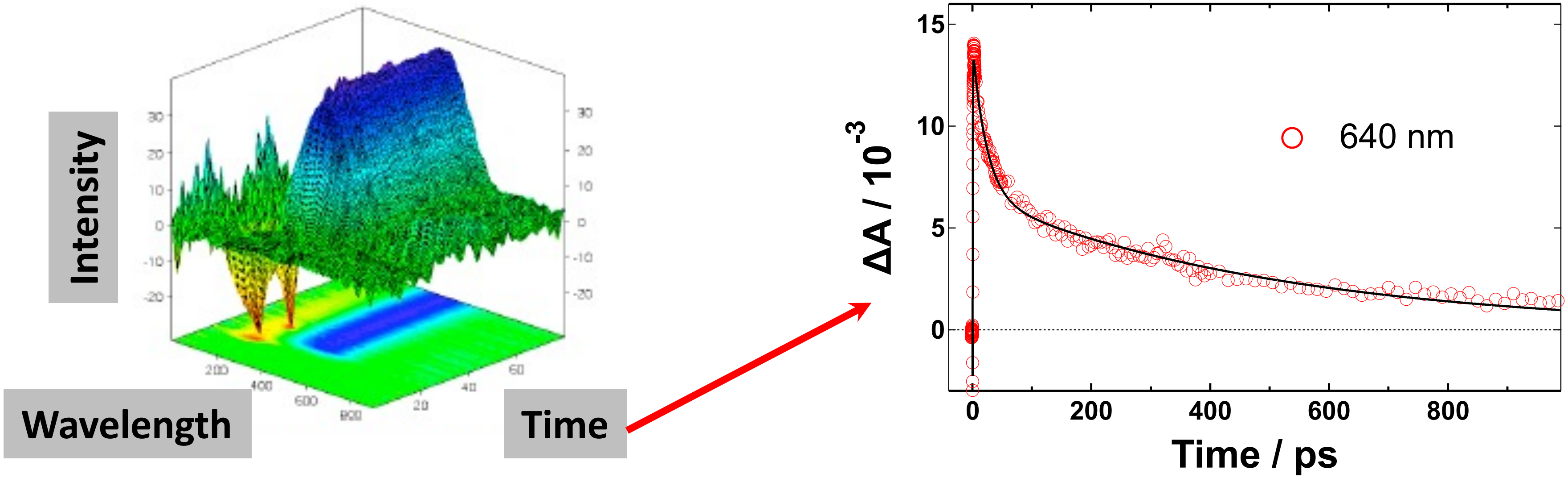
After pump excitation





Probe arrives after pump
Transient signal at Δt after excitation

Data analysis: Dynamics



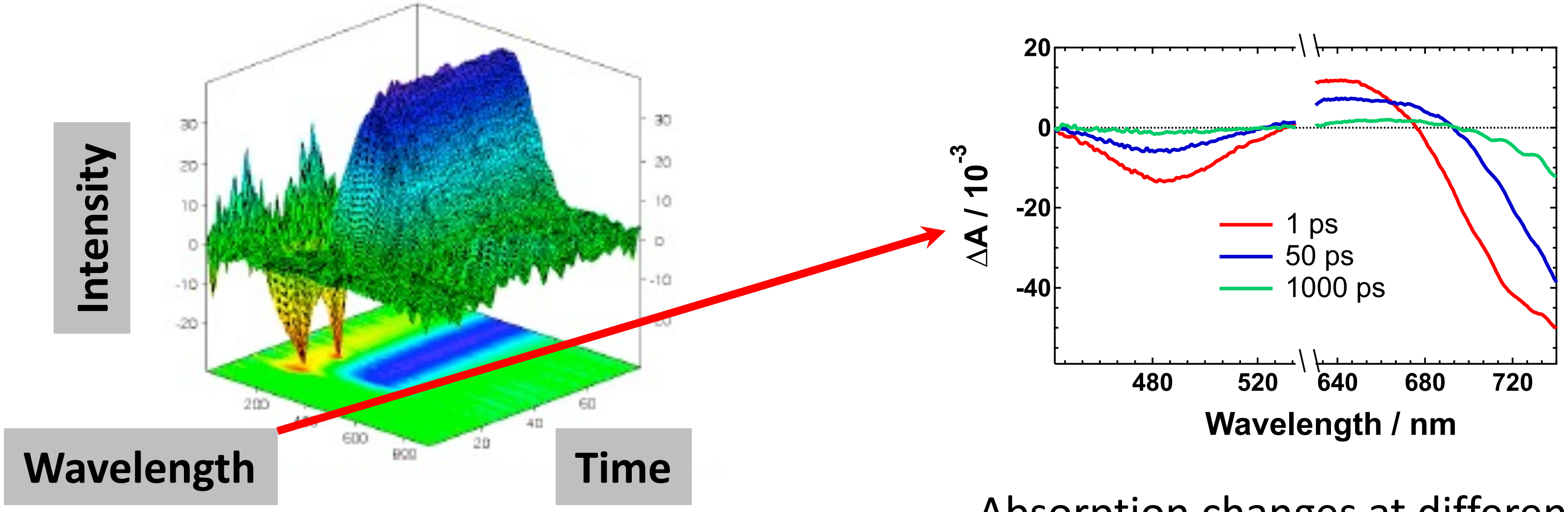
- Time-dependence at a specific wavelength
- Can selectively investigate the dynamic evolution of an excited state species
- Lifetime can be extracted from the fit of the time-evolution trace

$$\Delta A(t) = A_{pump} - A_{no\ pump} = \Delta A_0 \exp(-t/\tau)$$

Amplitude difference at t=0

Lifetime

Data analysis: Spectra



Absorption changes at different times after light excitation

NEGATIVE SIGNALS

$$\Delta A = -log\left(\frac{I_{T*}}{I_T}\right) < 0$$

$$I_{T*} > I_T$$

Ground state loss (="bleaching") or stimulated emission

POSITIVE SIGNALS

$$\Delta A = -log\left(\frac{I_{T*}}{I_T}\right) > 0$$

$$I_T > I_{T*}$$

Absorption from photoinduced species

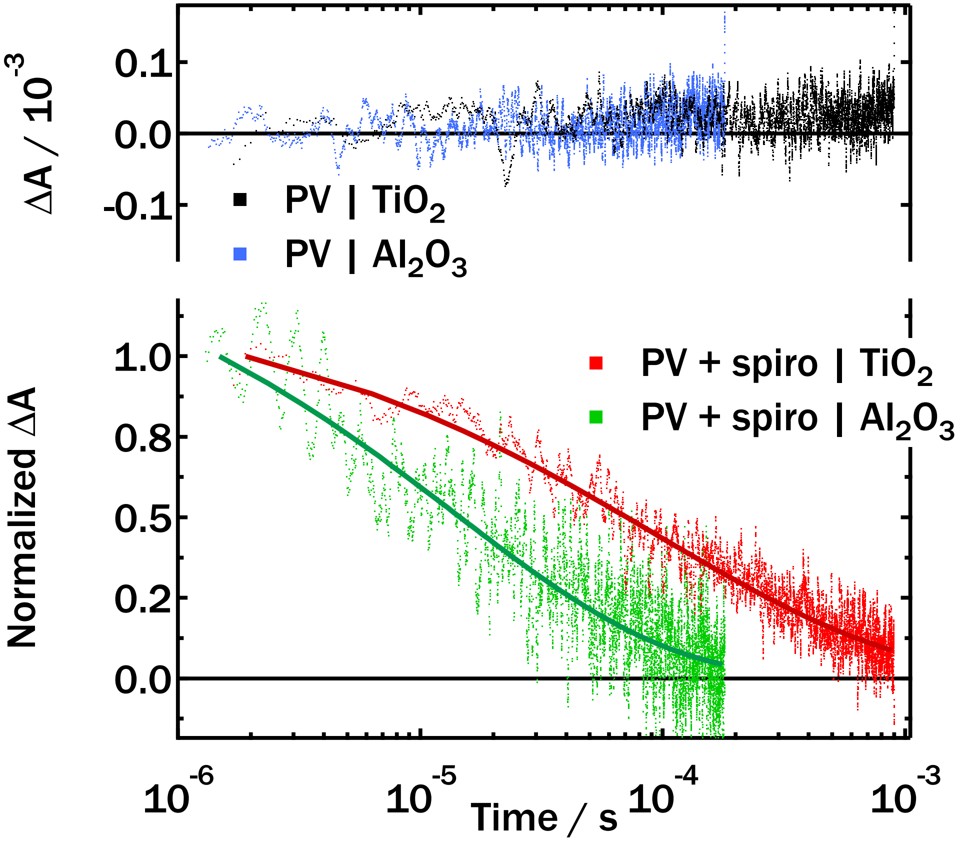
Why is this useful?

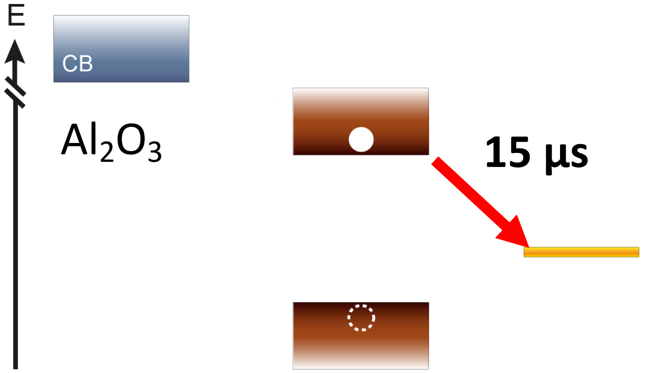
- Such techniques are extremely important to optimize solar cells and luminescent systems!

→ ***Investigate the competition between charge separation and charge recombination***

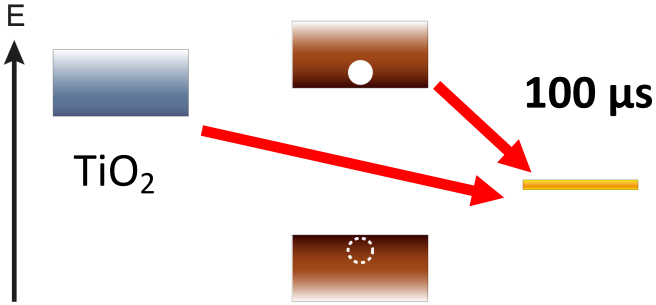
Interfaces: Charge Recombination

Transient absorption (example from last week)
Pump 580 nm
Probe 1400 nm: oxidized spiro





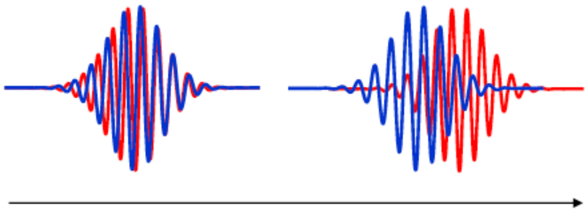
Stretched exponential
Broad distribution of distances between charges



Two heterojunctions help to separate the charges!

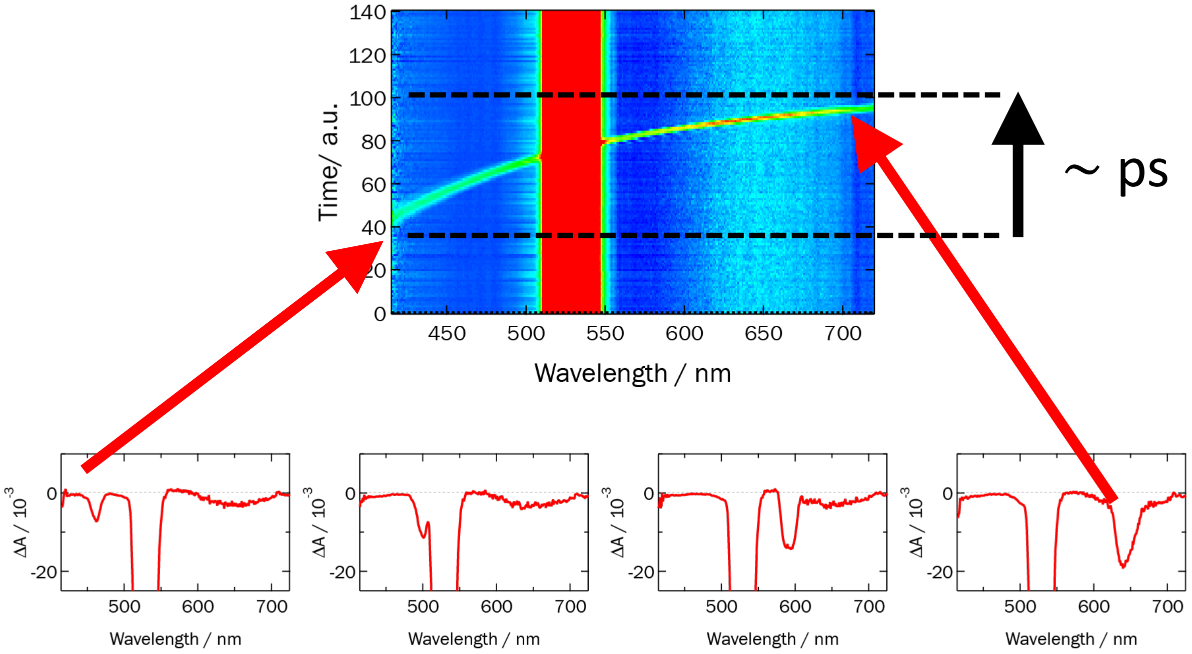
Fun things to see with TA…

This is a white light pulse “travelling in time” in a transparent medium:



$$\mathrm{v} = \frac{c}{n(\lambda)}$$

400 nm: 1.529, travels slower
600 nm: 1.516, travels faster



→ The red part of the spectrum has travelled 3 picoseconds faster than the blue part!
→ Ground velocity dispersion (GVD), may need to be corrected in the spectra