Ultrafast Spectroscopy

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XV Jorge Andre Swieca School on Nonlinear and Quantum Optics

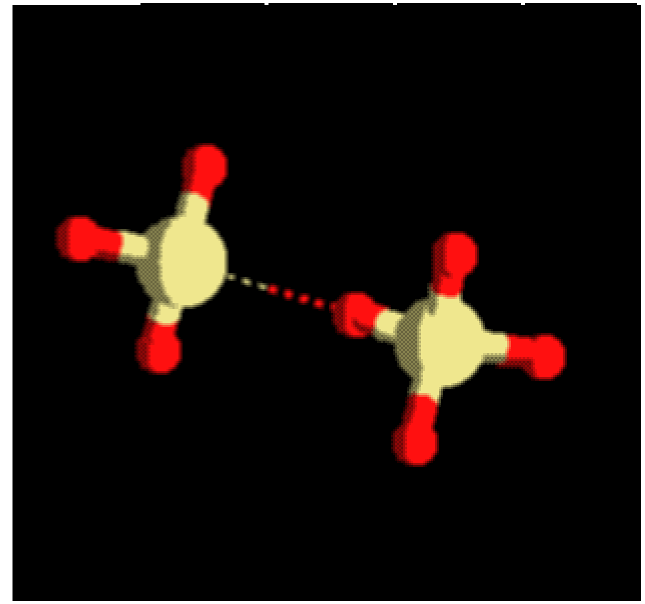
How Fast is Ultrafast?
Why Spectroscopy?
Ultrafast Laser Source
Pulsewidth Measurement
Simple Case – Transient Absorption
Examples
Reflection Spectroscopy
Transient Photoluminescence
Other Techniques
Take Home Message

Ultrafast Spectroscopy: Why?

Most events that occur in atoms and molecules occur on fs and ps time scales because the length scales are very small.

Fluorescence occurs on a ns time scale, but competing non-radiative processes only speed things up because relaxation rates add:

$$\boxed{1/\tau_{ex} = 1/\tau_{fl} + 1/\tau_{nr}}$$



Biologically important processes utilize excitation energy for purposes other than fluorescence and hence must be very fast.

Collisions in room-temperature liquids occur on a few-fs time scale, so nearly all processes in liquids are ultrafast.

Semiconductor processes of technological interest are necessarily ultrafast or we wouldn't be interested.

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From: Rick Trebino UFO course

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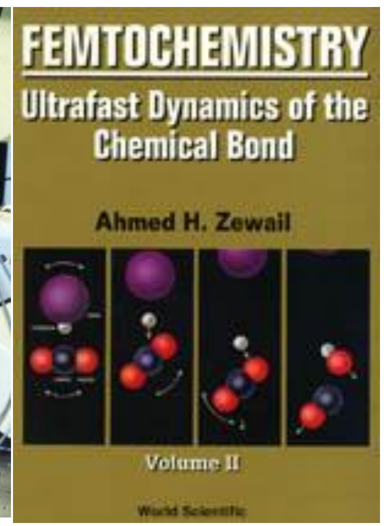
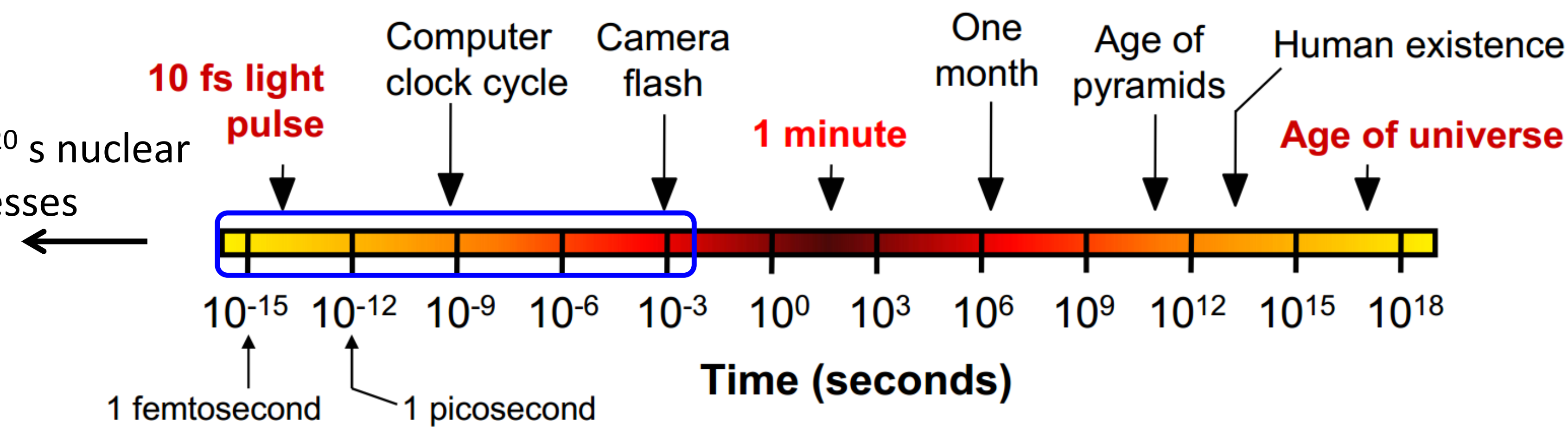
Ultrafast Spectroscopy: Why?



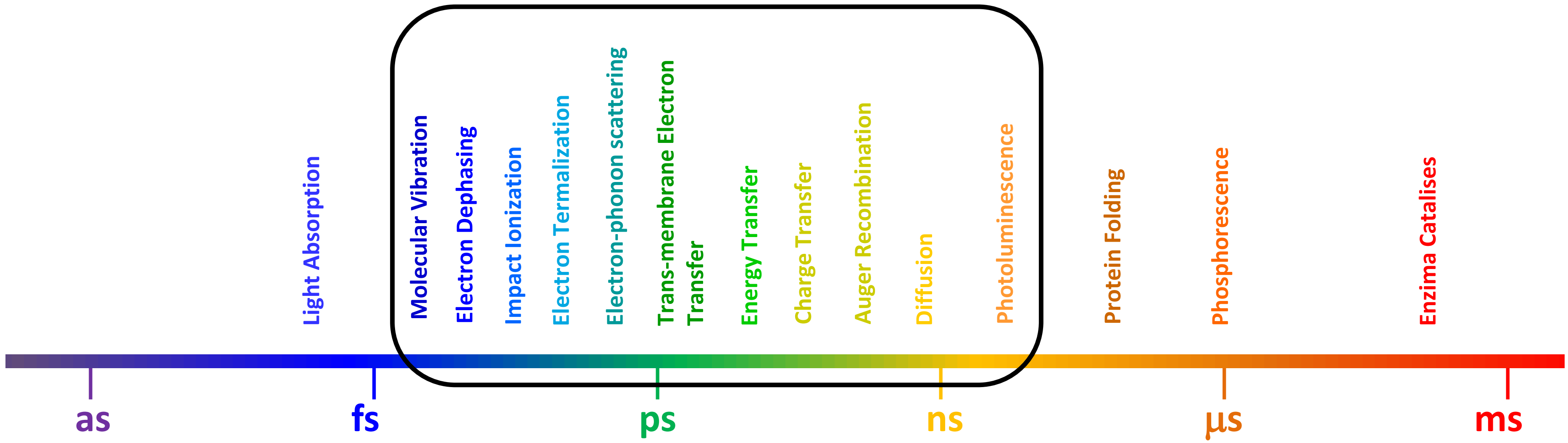
The 1999 Nobel Prize in Chemistry went to Professor Ahmed Zewail from CalTech for ultrafast spectroscopy.

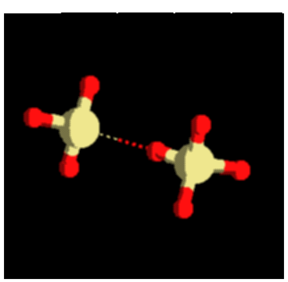
Time scale for natural occurring phenomena

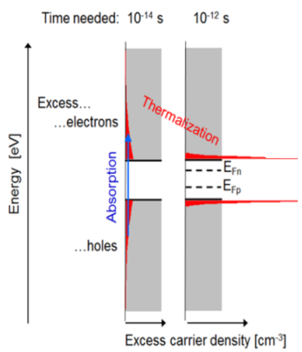
< 10^{-20} s nuclear processes

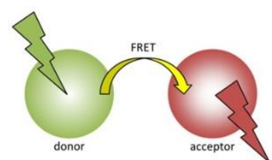


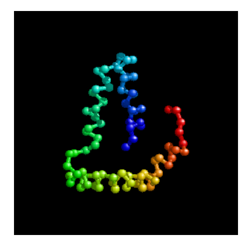
Time scale for natural occurring phenomena











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To measure those fast processes we need something even faster

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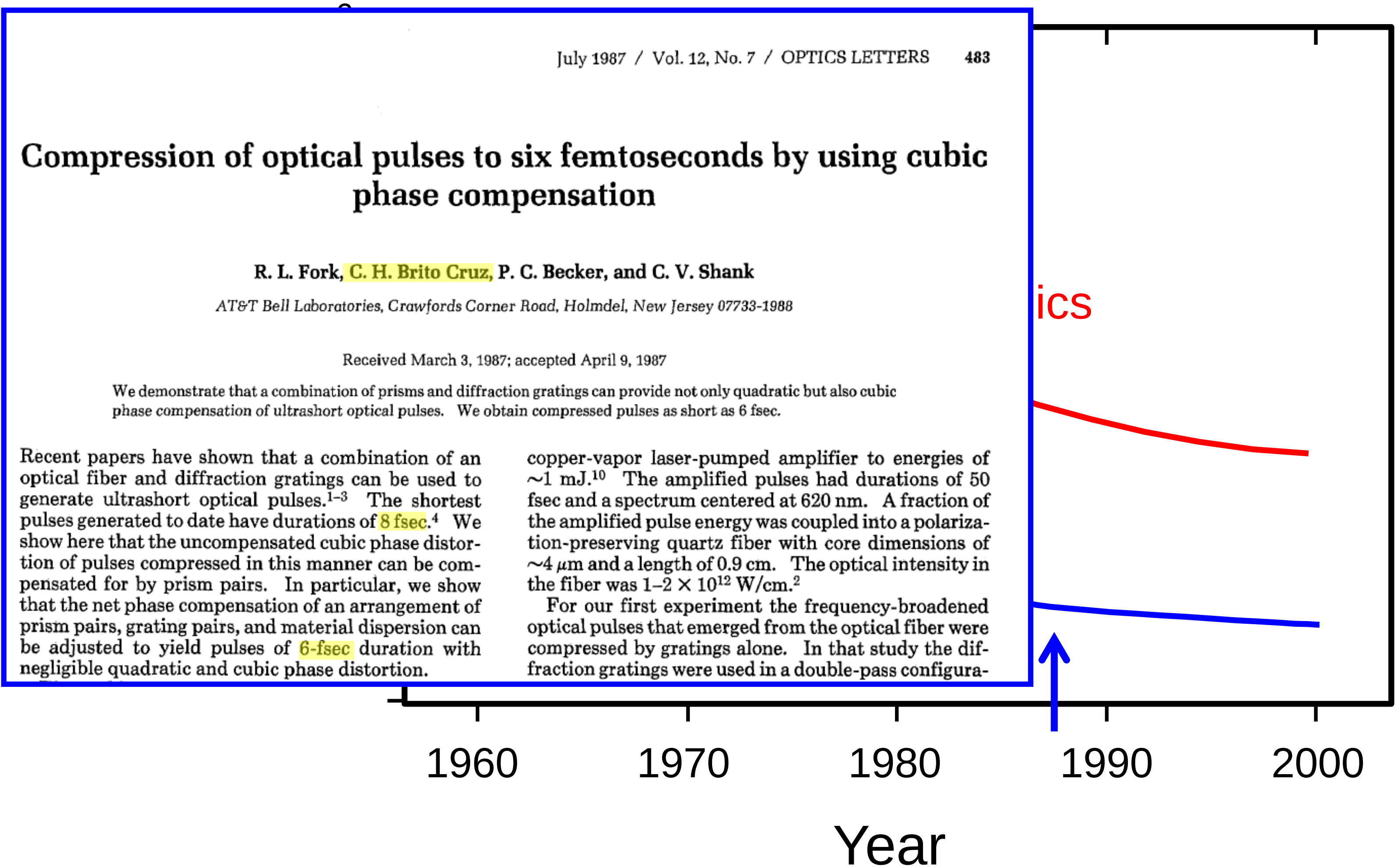
How can we measure things this fast?



July 1987 / Vol. 12, No. 7 / OPTICS LETTERS 483

Compression of optical pulses to six femtoseconds by using cubic phase compensation

R. L. Fork, C. H. Brito Cruz, P. C. Becker, and C. V. Shank

AT&T Bell Laboratories, Crawfords Corner Road, Holmdel, New Jersey 07733-1988

Received March 3, 1987; accepted April 9, 1987

We demonstrate that a combination of prisms and diffraction gratings can provide not only quadratic but also cubic phase compensation of ultrashort optical pulses. We obtain compressed pulses as short as 6 fsec.

Recent papers have shown that a combination of an optical fiber and diffraction gratings can be used to generate ultrashort optical pulses.[1–3] The shortest pulses generated to date have durations of 8 fsec.[4] We show here that the uncompensated cubic phase distortion of pulses compressed in this manner can be compensated for by prism pairs. In particular, we show that the net phase compensation of an arrangement of prism pairs, grating pairs, and material dispersion can be adjusted to yield pulses of 6-fsec duration with negligible quadratic and cubic phase distortion.

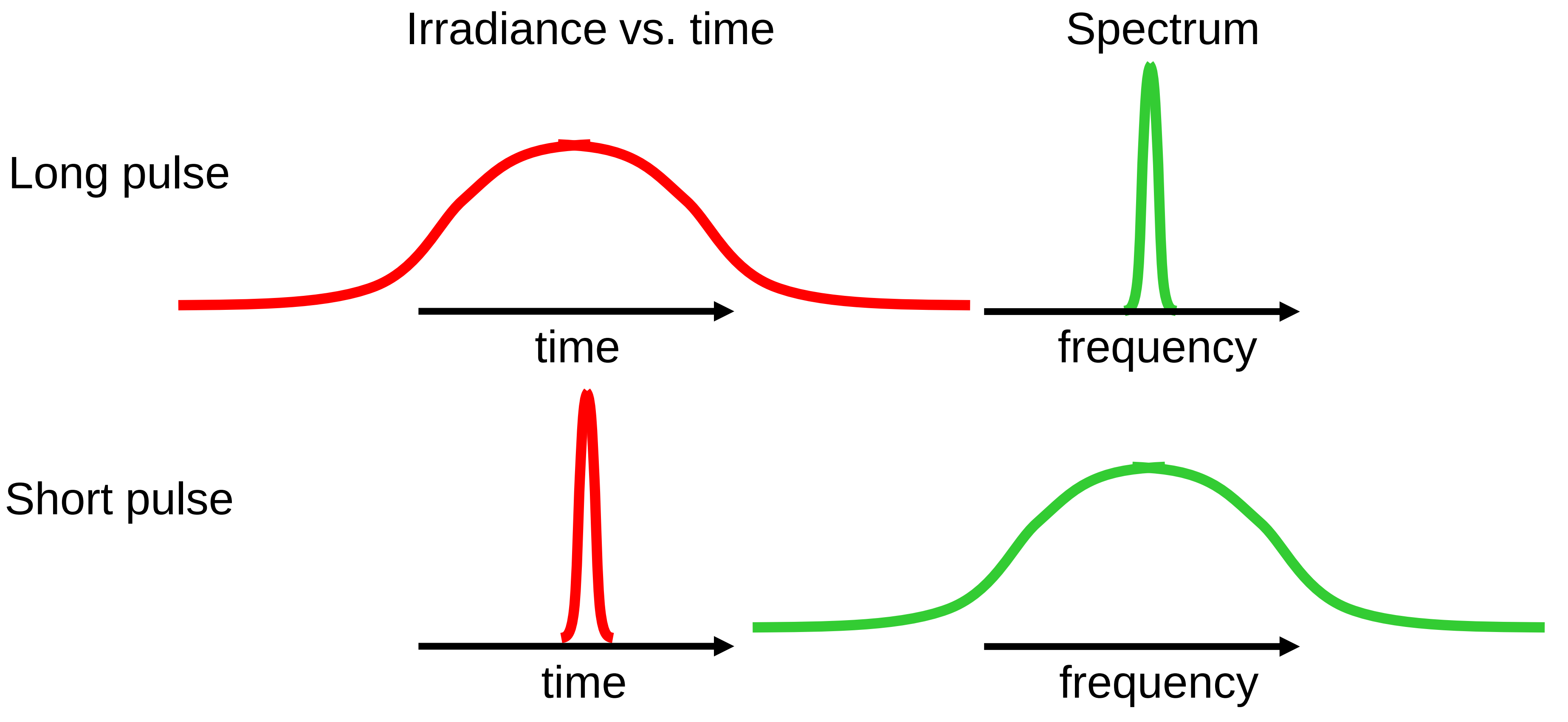
copper-vapor laser-pumped amplifier to energies of ~1 mJ.[10] The amplified pulses had durations of 50 fsec and a spectrum centered at 620 nm. A fraction of the amplified pulse energy was coupled into a polarization-preserving quartz fiber with core dimensions of ~4 μm and a length of 0.9 cm. The optical intensity in the fiber was 1–2 × 10^{12} W/cm.[2]

For our first experiment the frequency-broadened optical pulses that emerged from the optical fiber were compressed by gratings alone. In that study the diffraction gratings were used in a double-pass configura-

To date, mostly used laser source for ultrafast spectroscopy have 10 -100 fs pulsewidth

Ultrafast Laser: a bunch of lasers put together

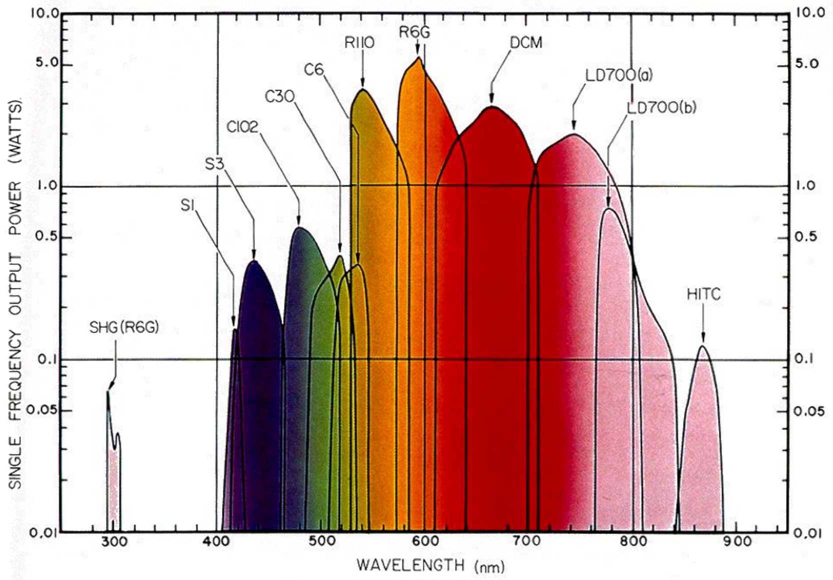
The uncertainty principle says that the product of the temporal and spectral pulse widths is greater than ~1.

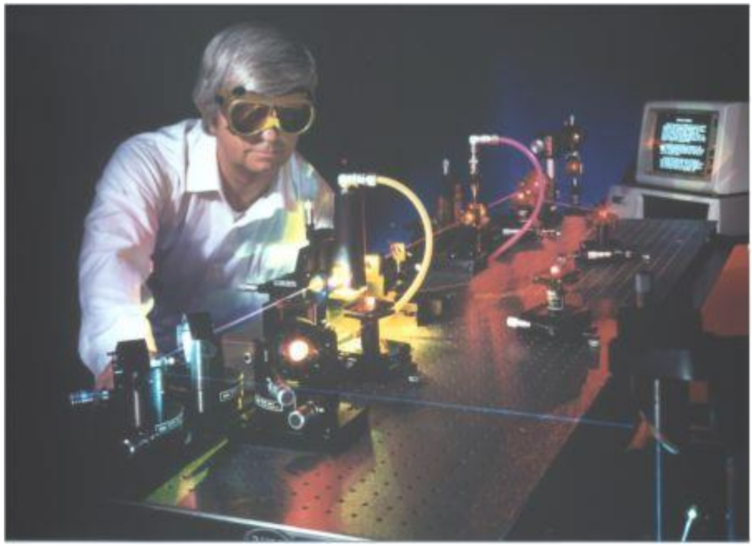


There is no single wavelength ultrafast laser!

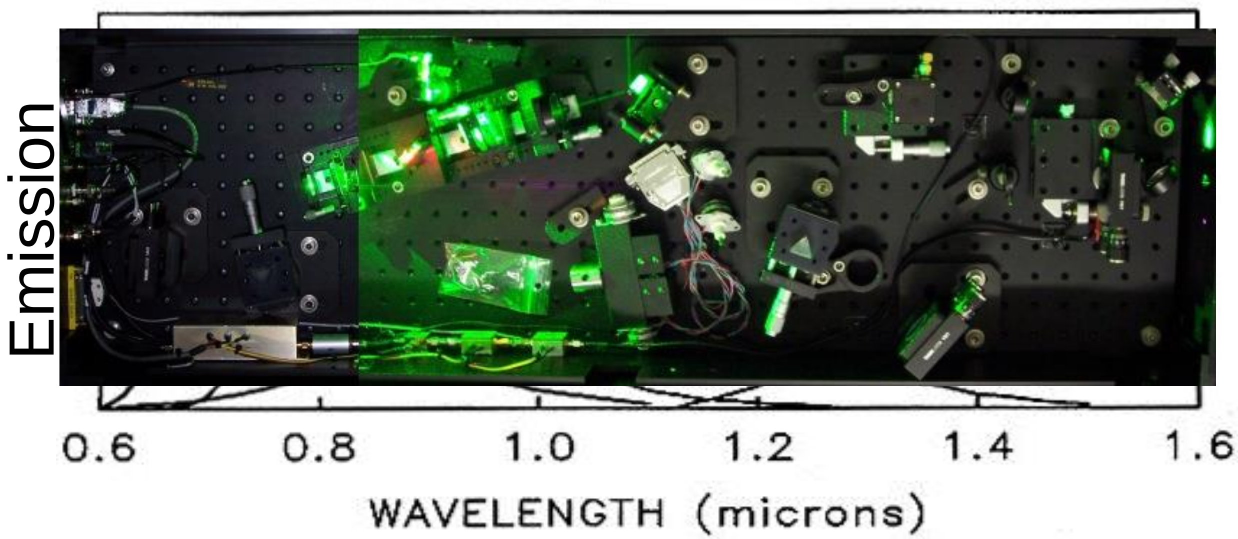
Ultrafast Laser: a bunch of lasers put together

For decades, ultrafast lasers were dye-based





Solid-state laser media have broad bandwidths and are convenient.



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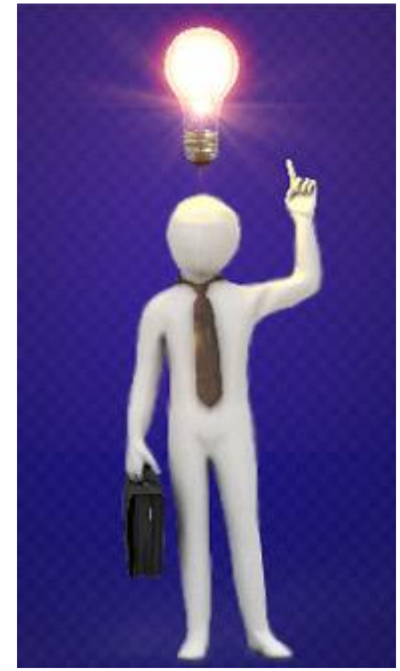
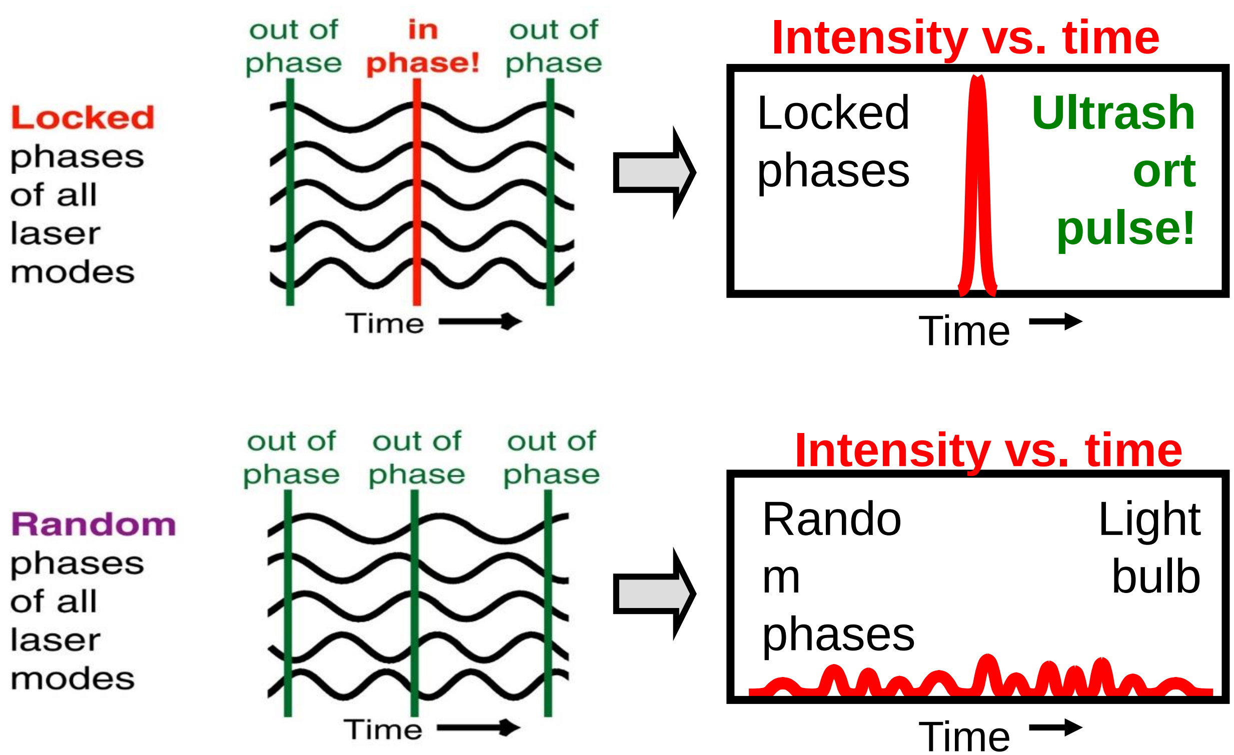
Ultrafast Laser: a bunch of lasers put together

A lamp also is broadband!

Why is it not ultrafast?



Mode-lock



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Ultrafast Laser: a bunch of lasers put together

What are those mode?

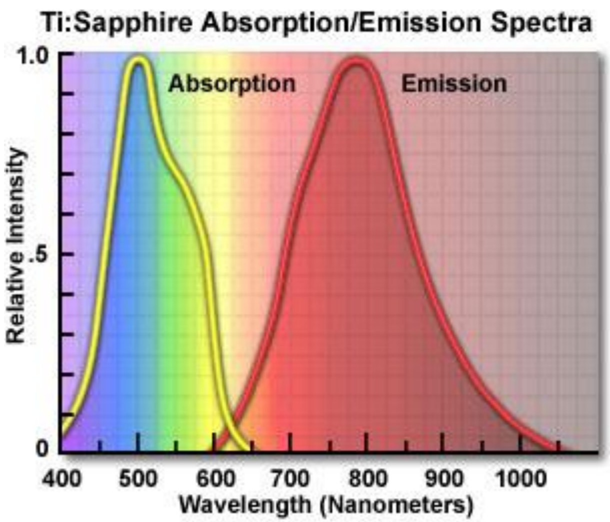
$$\omega_n = 2\pi n \frac{c}{2L}$$

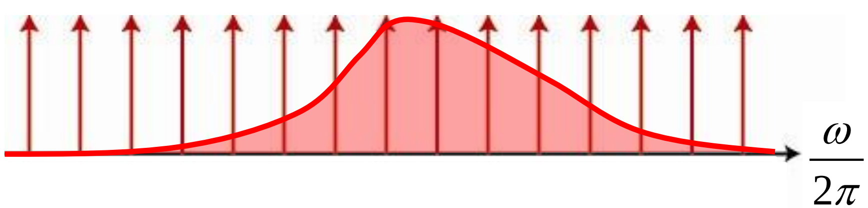
L = Cavity length

n = interger

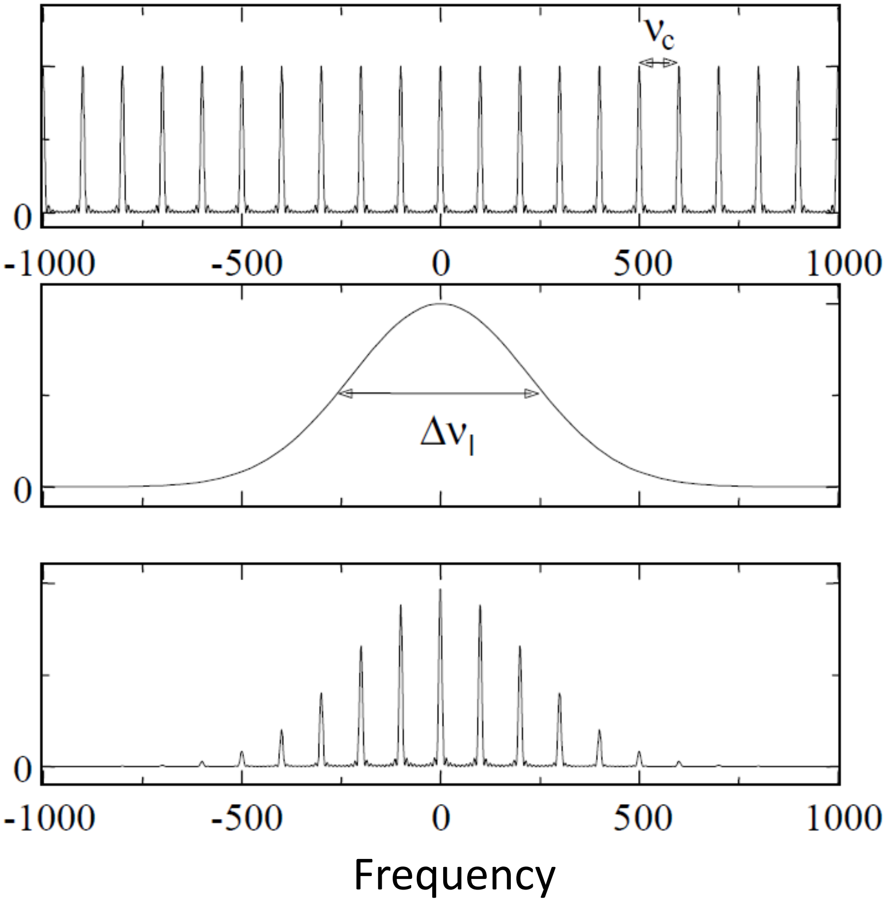
For a 2 m cavity Ti:sapphire laser:

$$\omega_1 = 5 \times 10^8\, rad/s$$
$$\omega_2 = 10 \times 10^8 rad/s$$
$$\vdots$$
$$\omega_{795772} = 4 \times 10^{14} rad/s$$





Ultrafast Laser: a bunch of lasers put together



$$E(t) = \sum_{-\infty}^{\infty} E_n(t) \exp[i(2\pi\nu_n t + \phi(t))]$$

Assuming that the phases are all constant

$$E(t) = E_o \exp(iN\omega_c t) \left[\frac{\sin\left(\frac{N\omega_c t}{2}\right)}{\sin\left(\frac{w_c t}{2}\right)} \right]$$

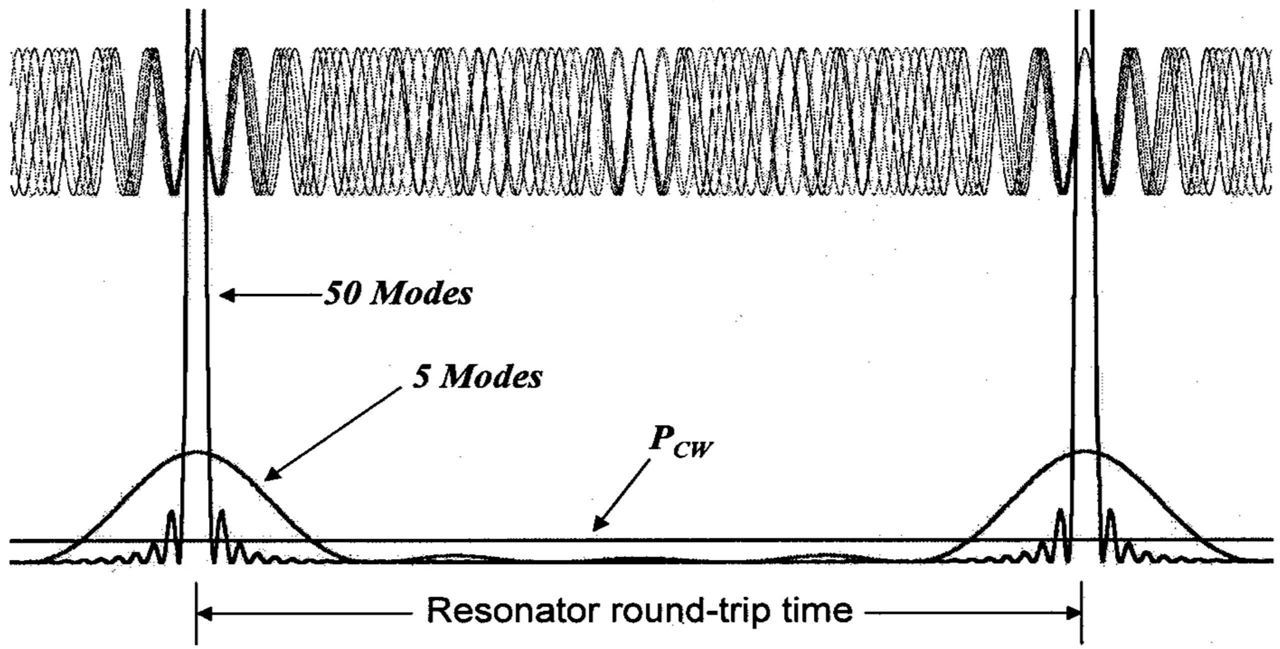
$$I(t) = I_0 \left[\frac{\sin\left(\frac{N\omega_c t}{2}\right)}{\sin\left(\frac{\omega_c t}{2}\right)} \right]^2$$

$$\boxed{\frac{1}{T_p} = \frac{N\omega_c}{2\pi} = \frac{N}{T_c}}$$

Pulse duration

Circulation time

Ultrafast Laser: a bunch of lasers put together



$$T_c = \frac{2L}{c} = \frac{2 \times 2\,m}{3 \times 10^8 m/s} \cong 12.5\,ns$$

Typical commercially available Ti:sapphire oscillator (rep rate = 80 MHz)

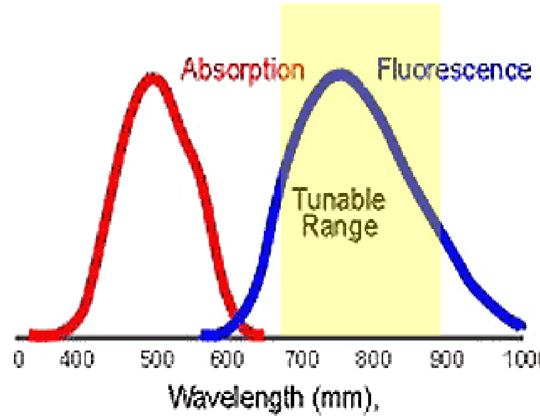
Didomenico, J. Appl. Phys. 35, 2870 (1964).
Hargrove, et al., Appl. Phys. Lett., 5, 4 (1964).

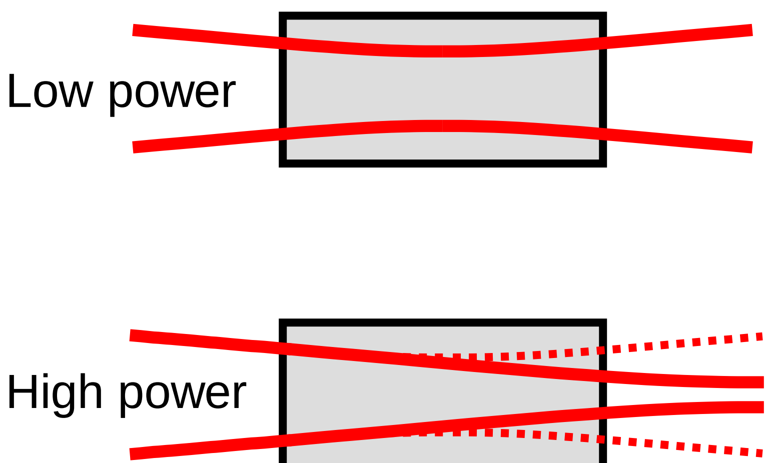
Ultrafast Laser: Ti:sapphire

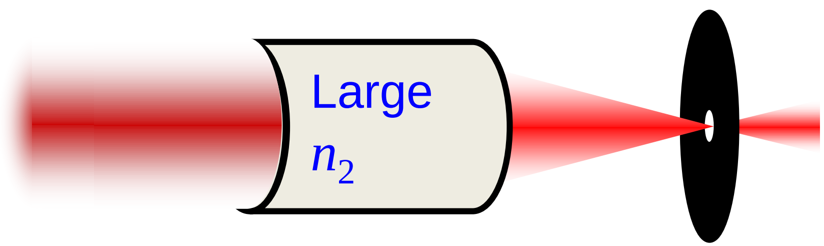
Oscillator

Ti:sapphire laser is the most widely used τ ~ 50 fs
Kerr Lens Modelocking

Ti:Sapphire not only lases, but it has a large n_2!







Only the high intensity part goes through the aperture.

Typical operation is at 80 MHz and 10 nJ per pulse – too fast and too low energy.

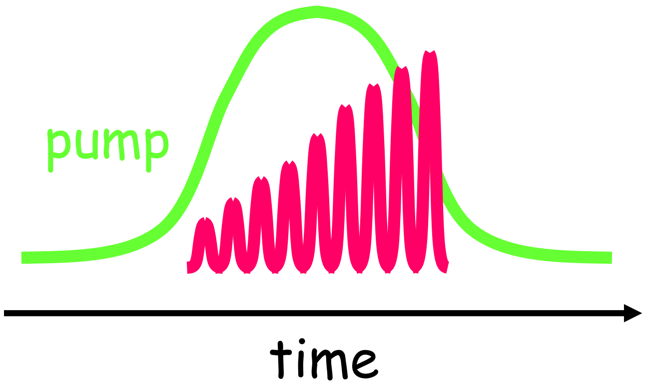
Ultrafast Laser: Ti:sapphire

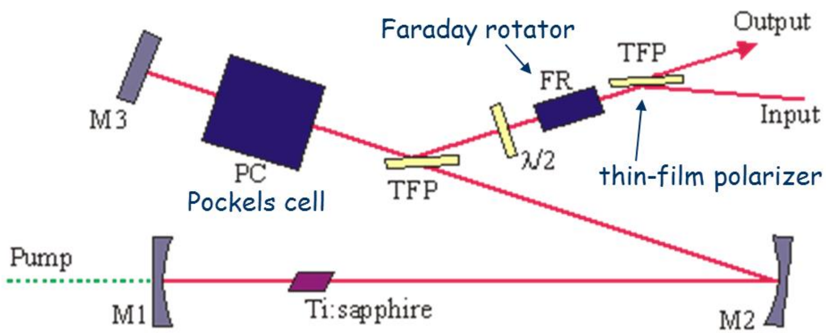
Amplifier

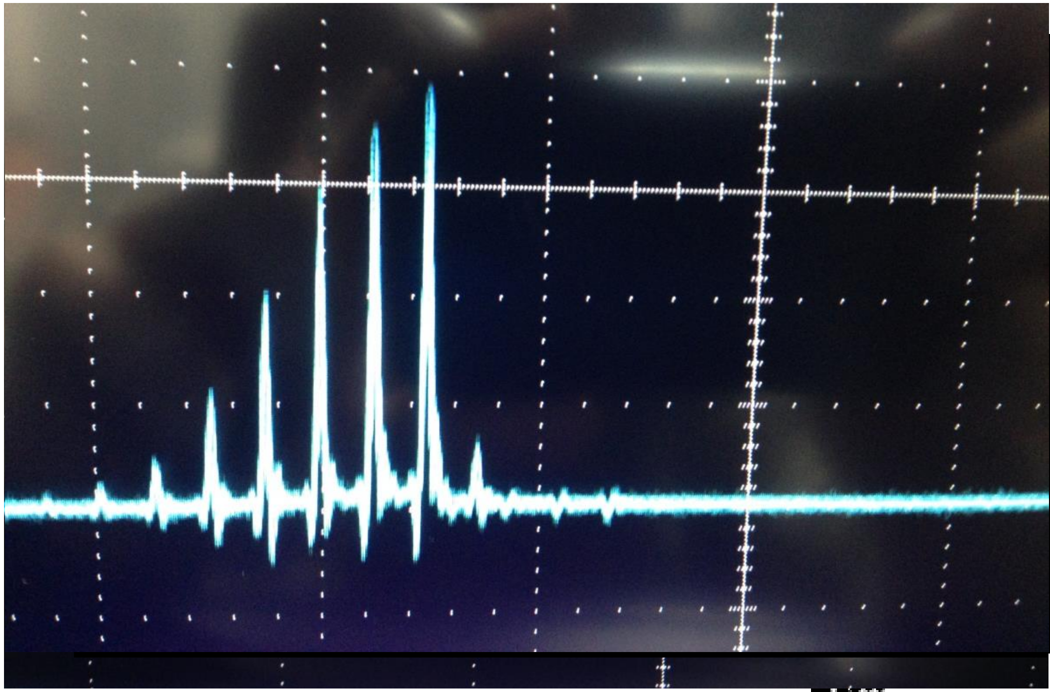
Ti:sapphire oscillator is used as the seed beam for the Ti:sapphire amplifier

Pump: Q-switched green laser – diode or flash lamp

Operation varies from single shot to nearly 1 MHZ







Ultrafast Laser: Ti:sapphire

Amplified Ti:sapphire laser – 1 kHz, 80 fs and 1 mJ per pulse

- 12.5 GW – peak power

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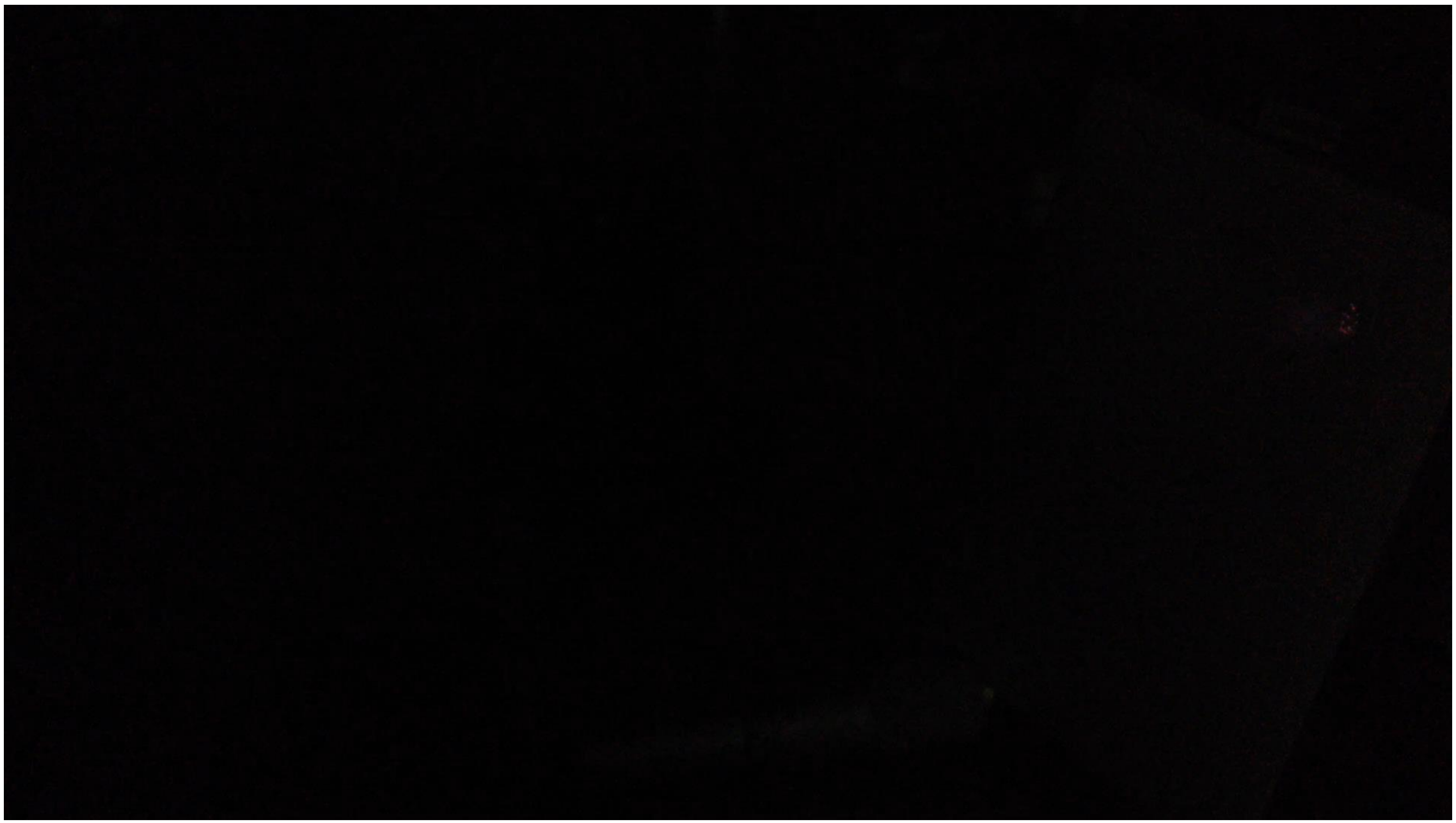
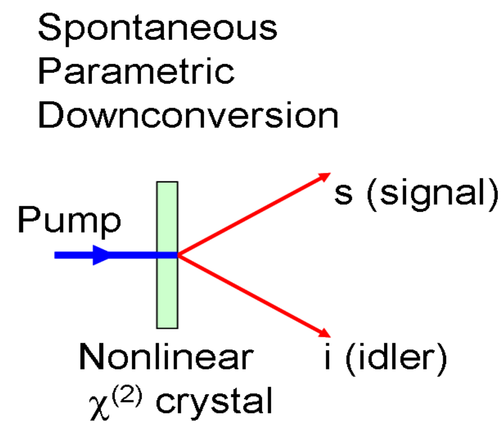


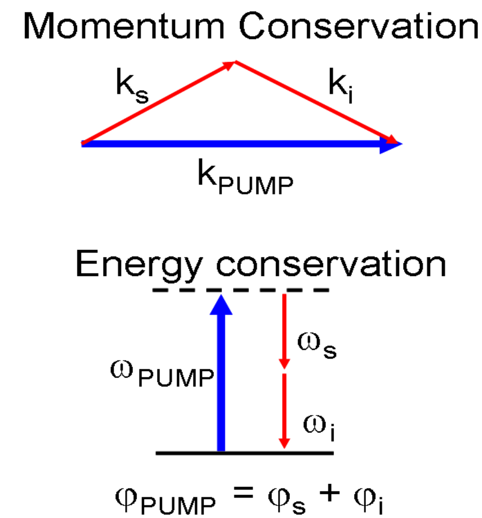
It really has the power!!!

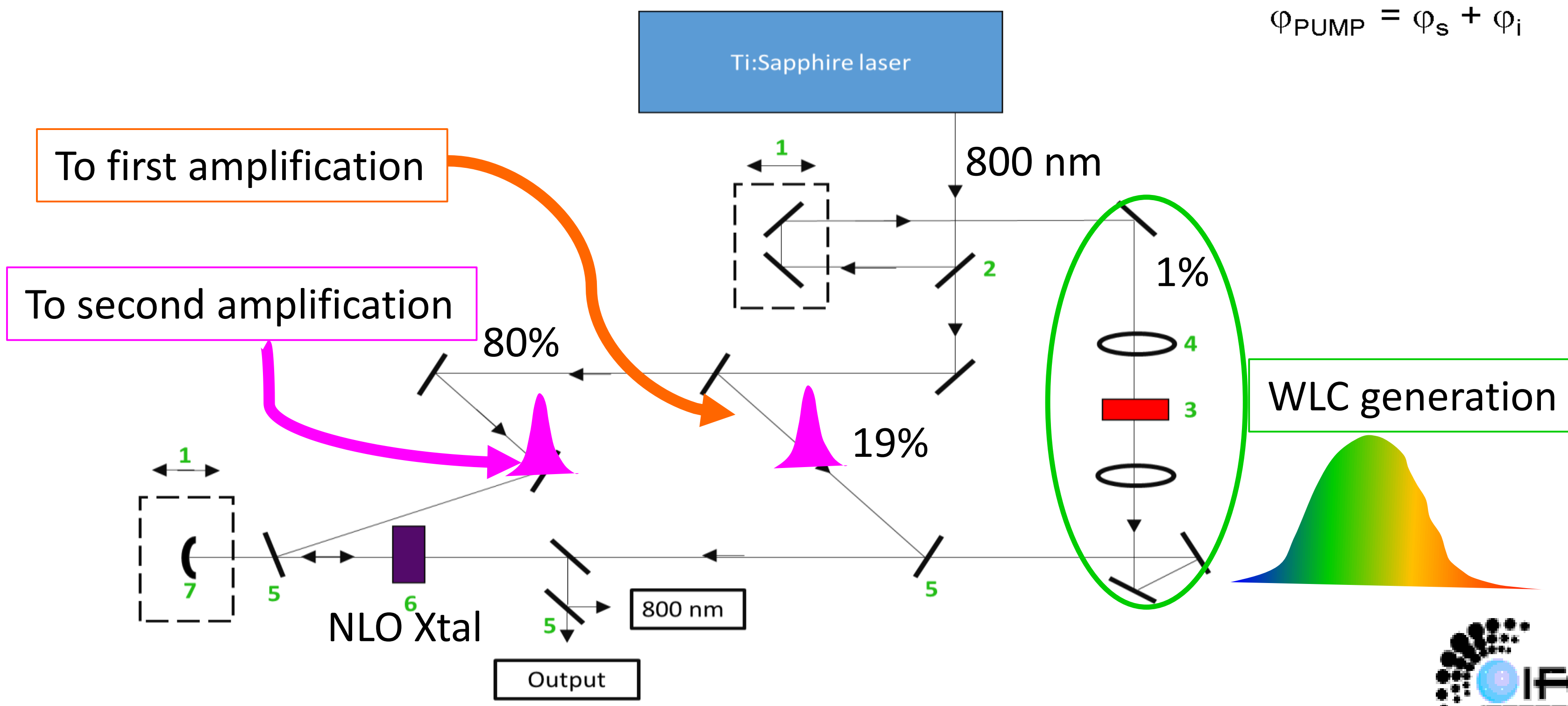
Easy to access the nonlinear optical regime

Ultrafast Laser : Tuning wavelengths

Nonlinear Optics

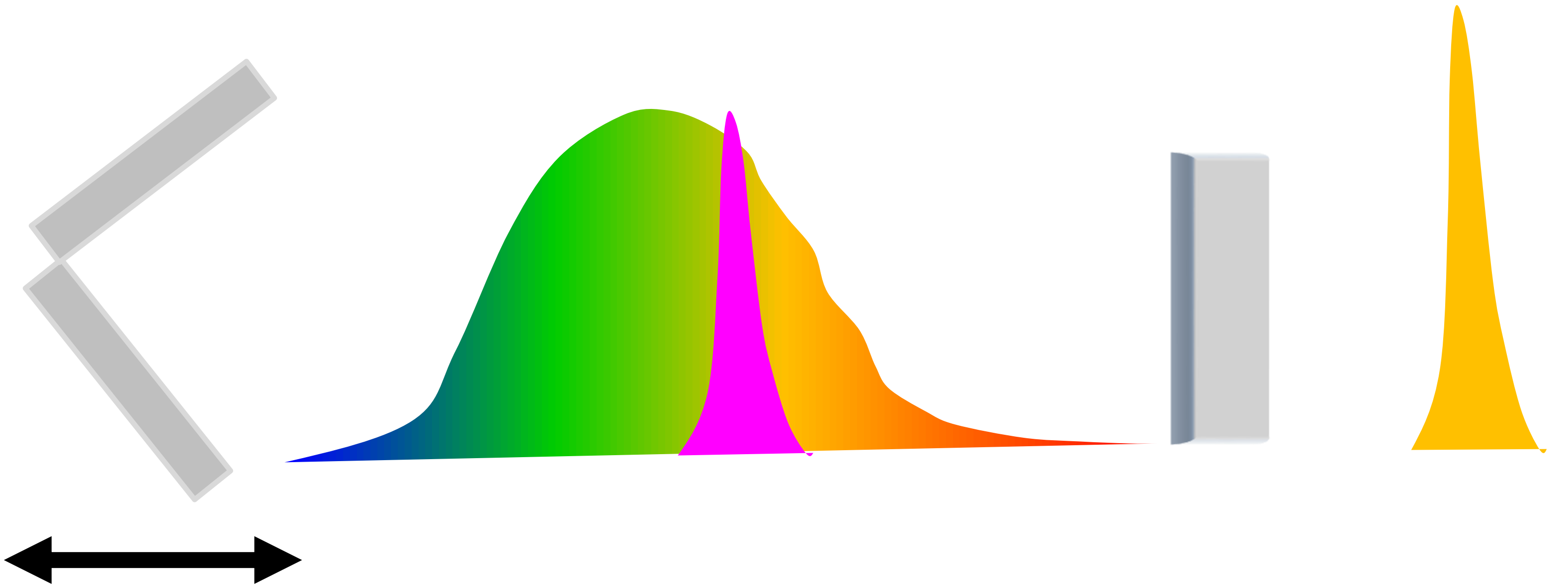






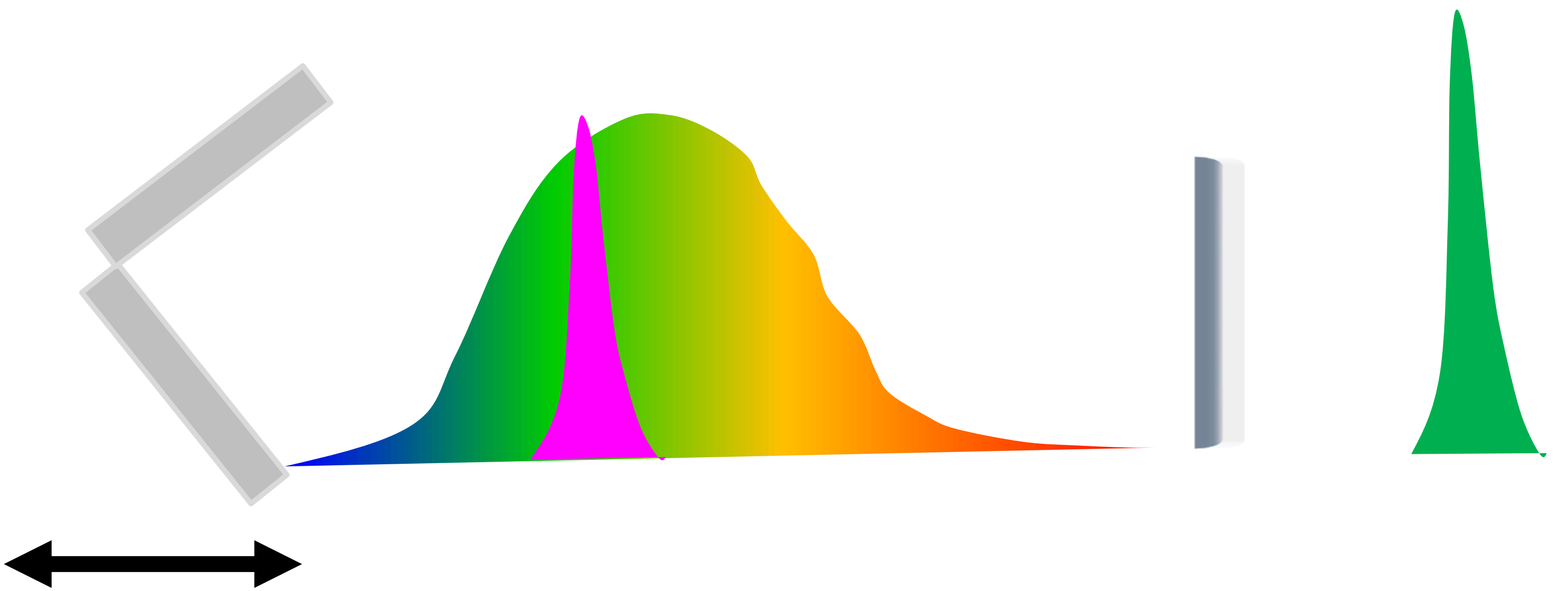
Ultrafast Laser : Tuning wavelengths

Nonlinear Optics



Ultrafast Laser : Tuning wavelengths

Nonlinear Optics



Ultrafast Laser : Tuning wavelengths

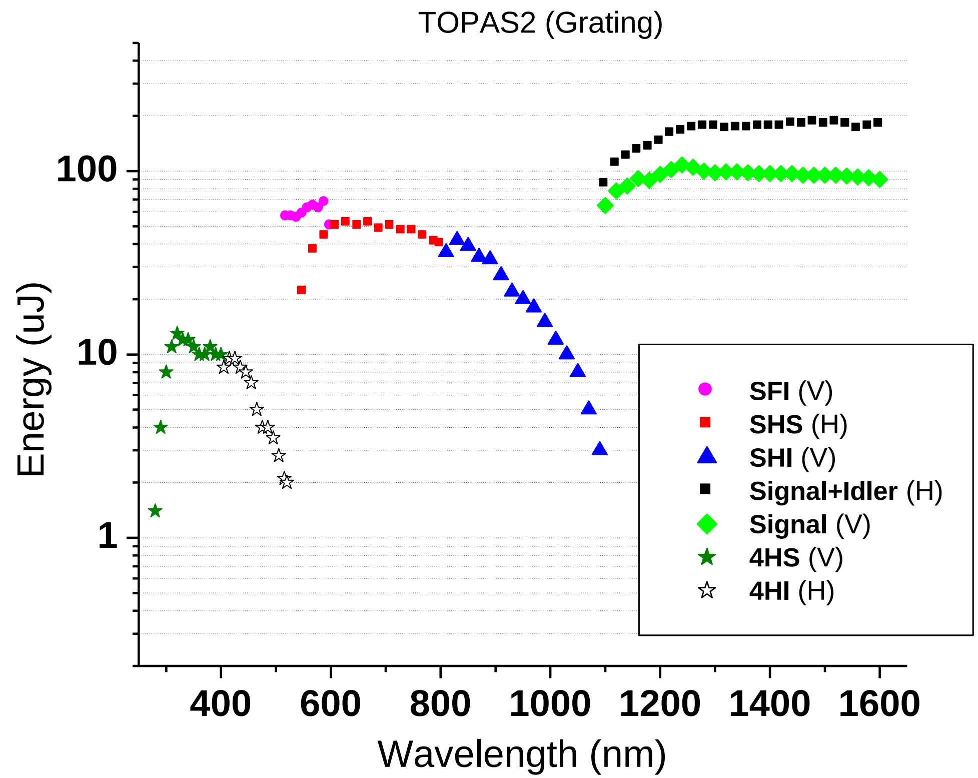
OPA

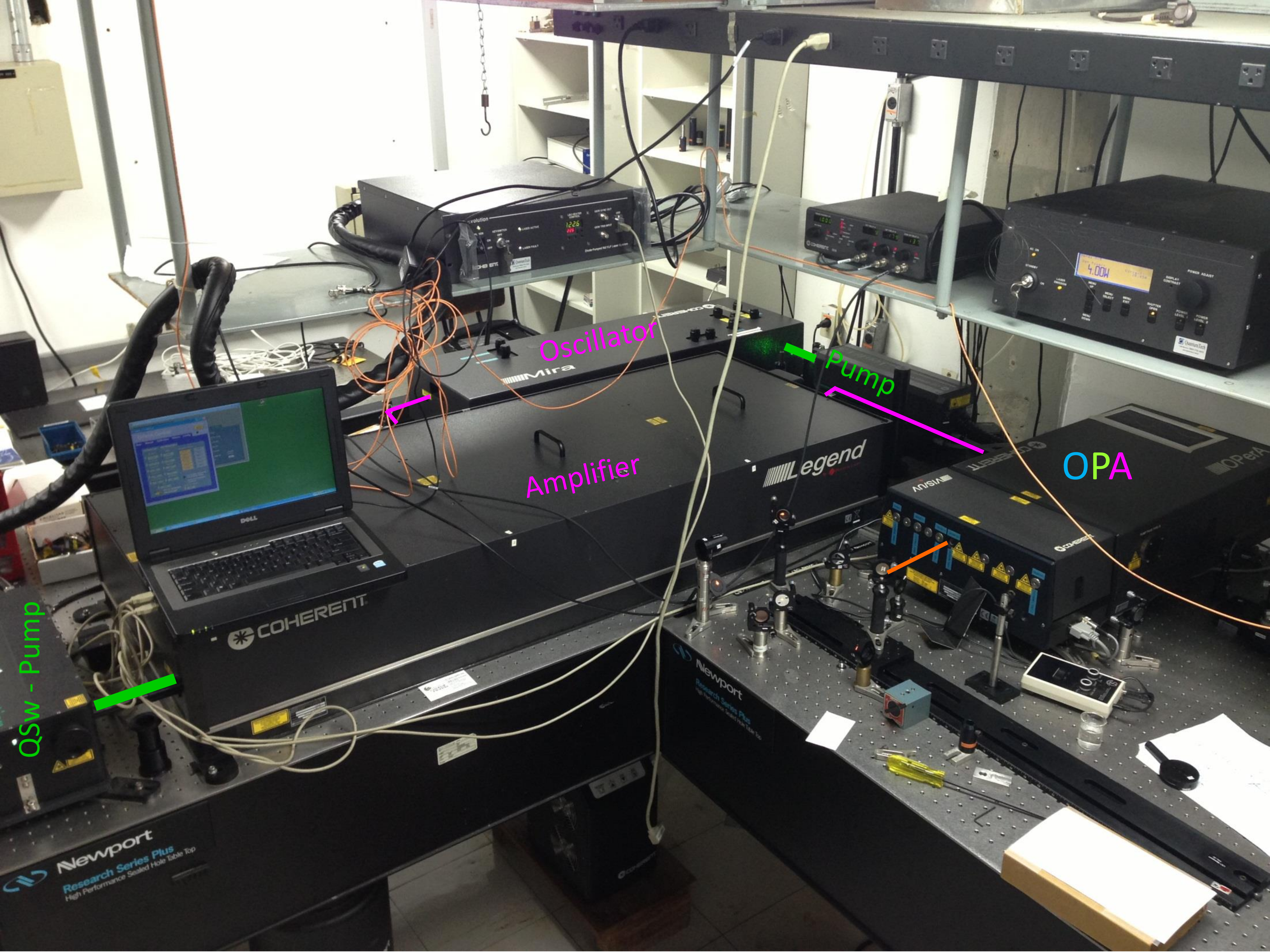
Ti:sapphire amplifiers typically operates at 800 nm

Ti:sapphire amplifiers are used to pump Optical Parametric Amplifiers

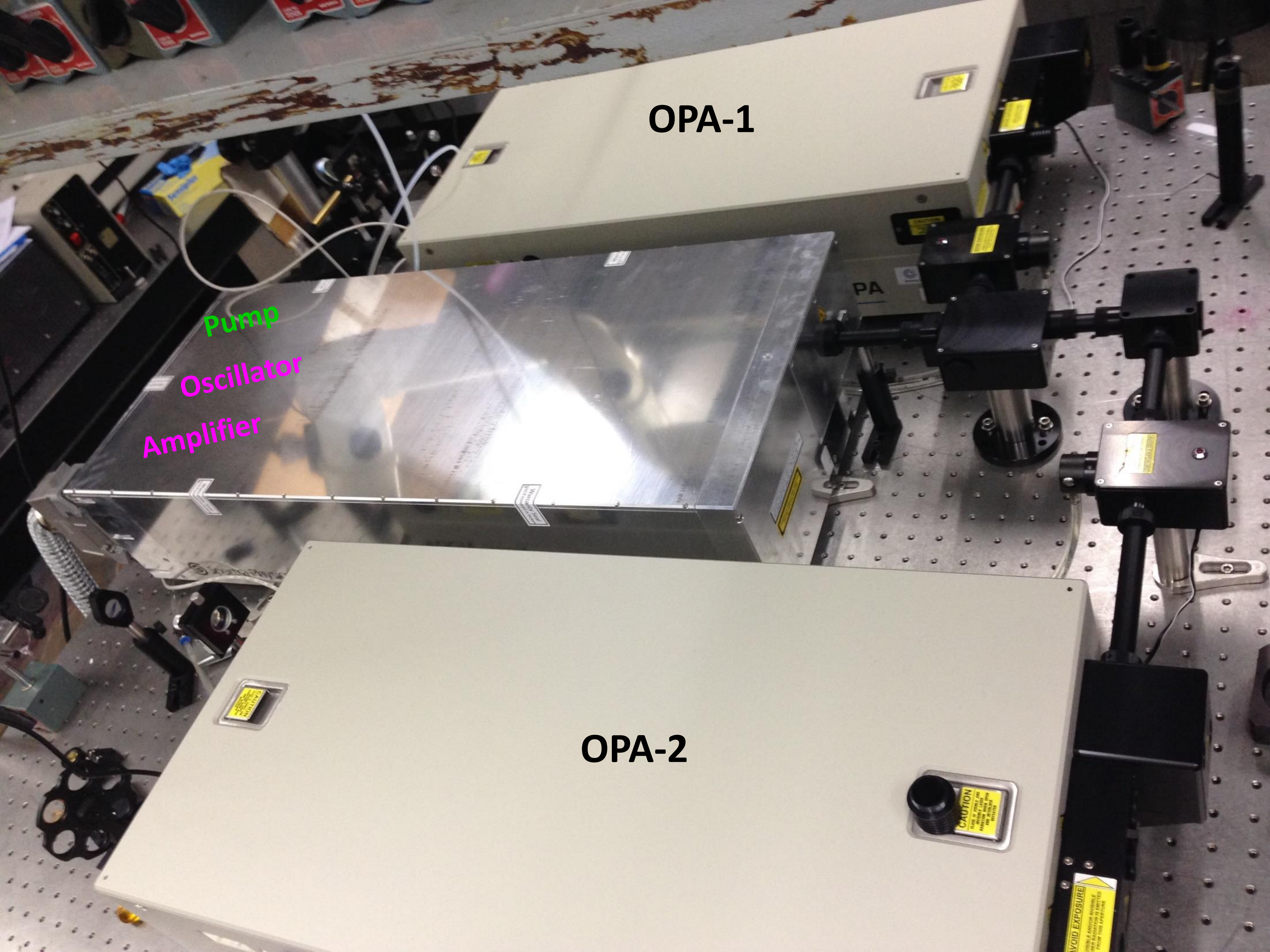
IR OPA´s are tunable from 1100 nm – 2600 nm.

SHG, SFG, DFG, FHG can be used to cover from ~300 nm to 10 μm.



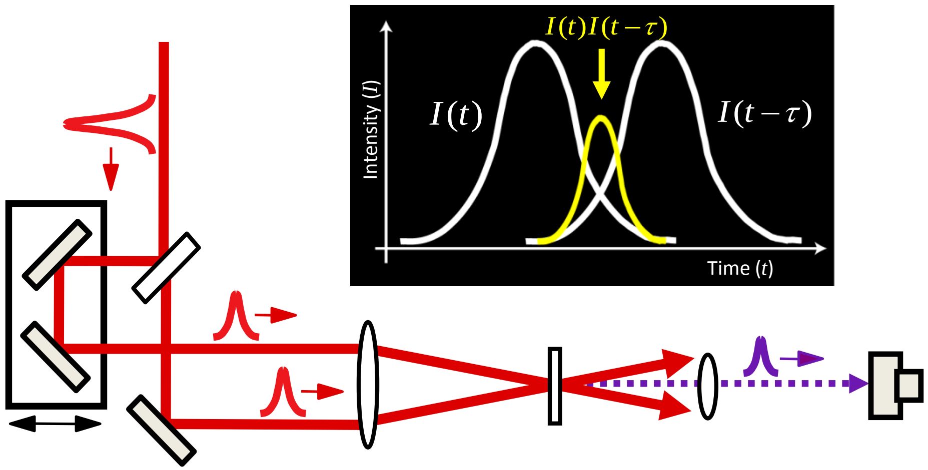


Oscillator
Mira
Pump
Amplifier
Legend
OPA
OPerA
COHERENT
QSw - Pump
Newport
Research Series Plus
High Performance Sealed Hole Table Top


OPA-1
Pump
Oscillator
Amplifier
OPA-2

Pulse Width Measurement

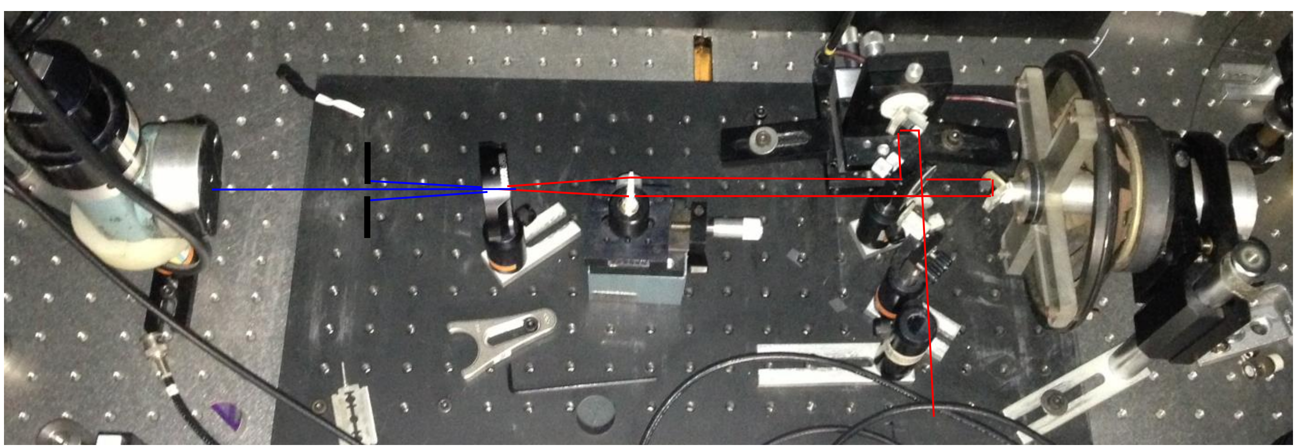
To measure something fast, we need something even faster!!!! – **Nonlinear optics**



Autocorrelation by SHG – tracks only intensity

$$A^{(2)}(\tau) \equiv \int_{-\infty}^{\infty} I(t) I(t-\tau)\, dt$$

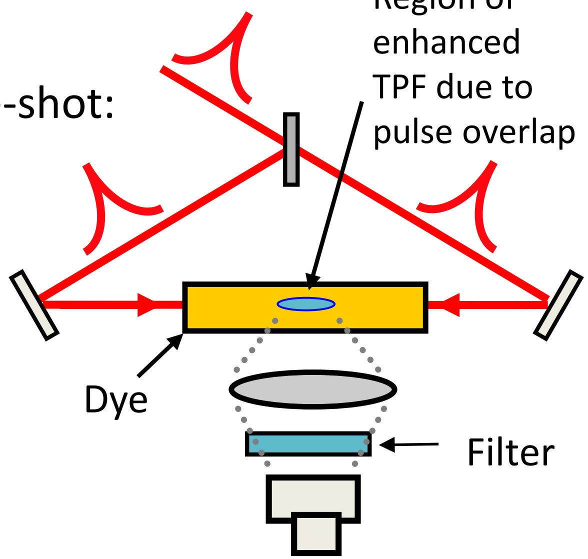
Real time pulse width monitoring using a speaker



Pulse Width Measurement – Other Methods

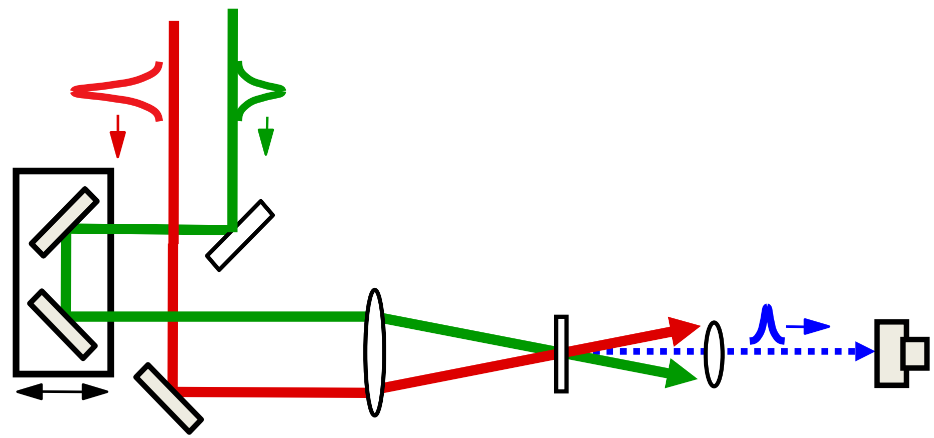
Two-Photon Fluorescence

Single-shot:



Real time monitoring

Sum Frequency Generation



Strong and stable reference pulse is used to SFG with the unknown pulse

Direct Two-Photon-Absorption in Photodiodes

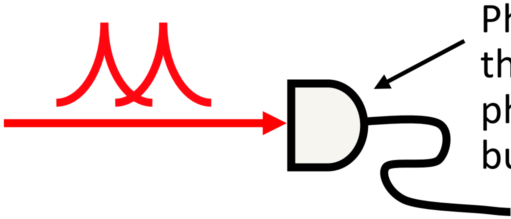


Photo-detector that absorbs two photons of ω each, but not one at ω.

Need scanning

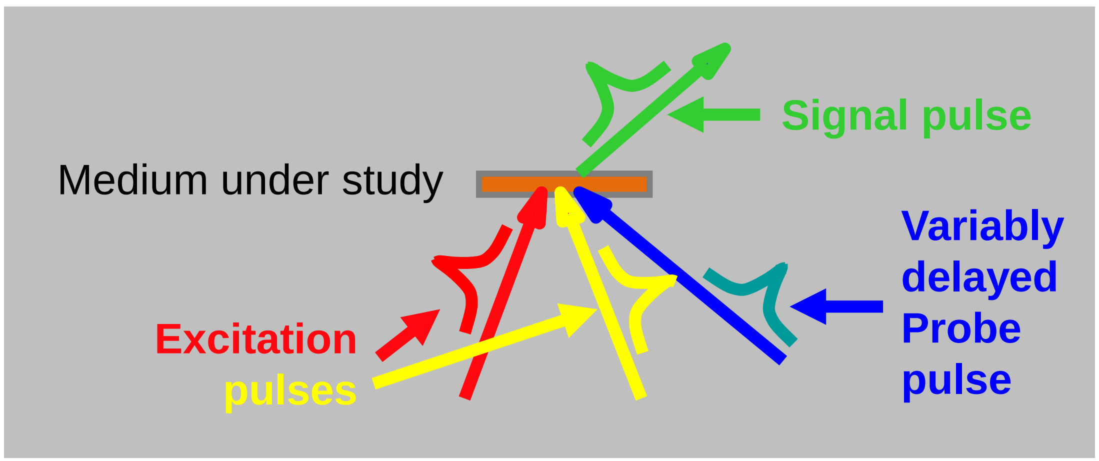
Other Methods

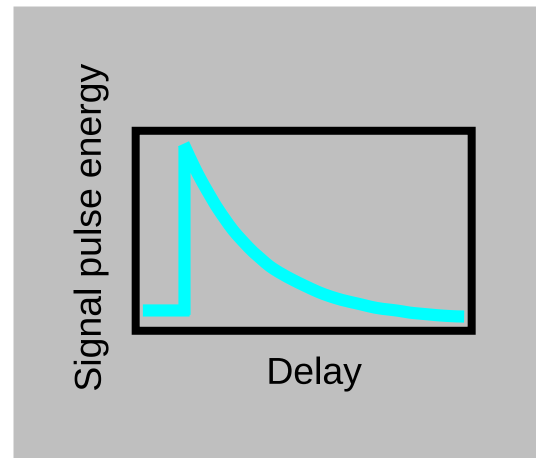
- FROG
- Interferometric Autocorrelator
- Polarization Autocorrelator - OKE

Ultrafast Spectroscopy: How?

Ultrafast laser spectroscopy involves studying ultrafast events that take place in a medium using ultrashort pulses and **delays** for time resolution.

It usually involves exciting the medium with one (or more) ultrashort laser pulse(s) and probing it a variable delay later with another.





The signal pulse energy (or change in energy) is plotted vs. delay.

The experimental temporal resolution is the pulse length.

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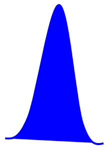
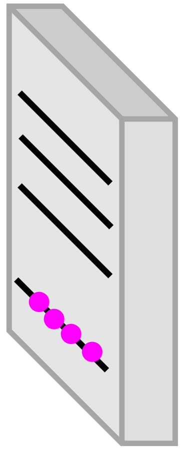
Principles of Ultrafast Spectroscopy

Study **ultrafast events** which takes place in materials upon interaction with photons, using lasers with **ultrashort pulses** and **delay stages** for time resolution





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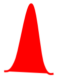
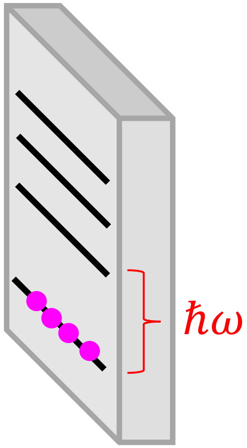




Pump pulse changes the population distribution and consequently,

Changes the absorption cross section

Principles of Ultrafast Spectroscopy

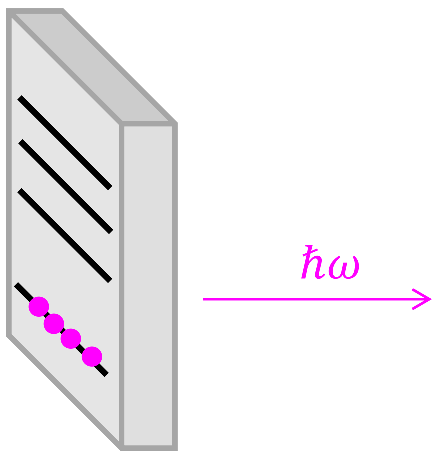
Study **ultrafast events** which takes place in materials upon interaction with photons, using lasers with **ultrashort pulses** and **delay stages** for time resolution

Pump pulse changes the population distribution and consequently,

Changes the absorption cross section
Changes the refractive index

Principles of Ultrafast Spectroscopy

Study **ultrafast events** which takes place in materials upon interaction with photons, using lasers with **ultrashort pulses** and **delay stages** for time resolution

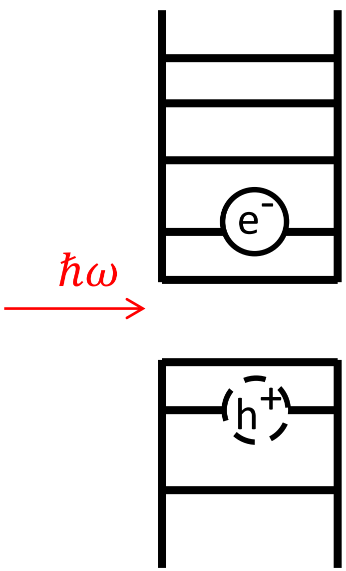


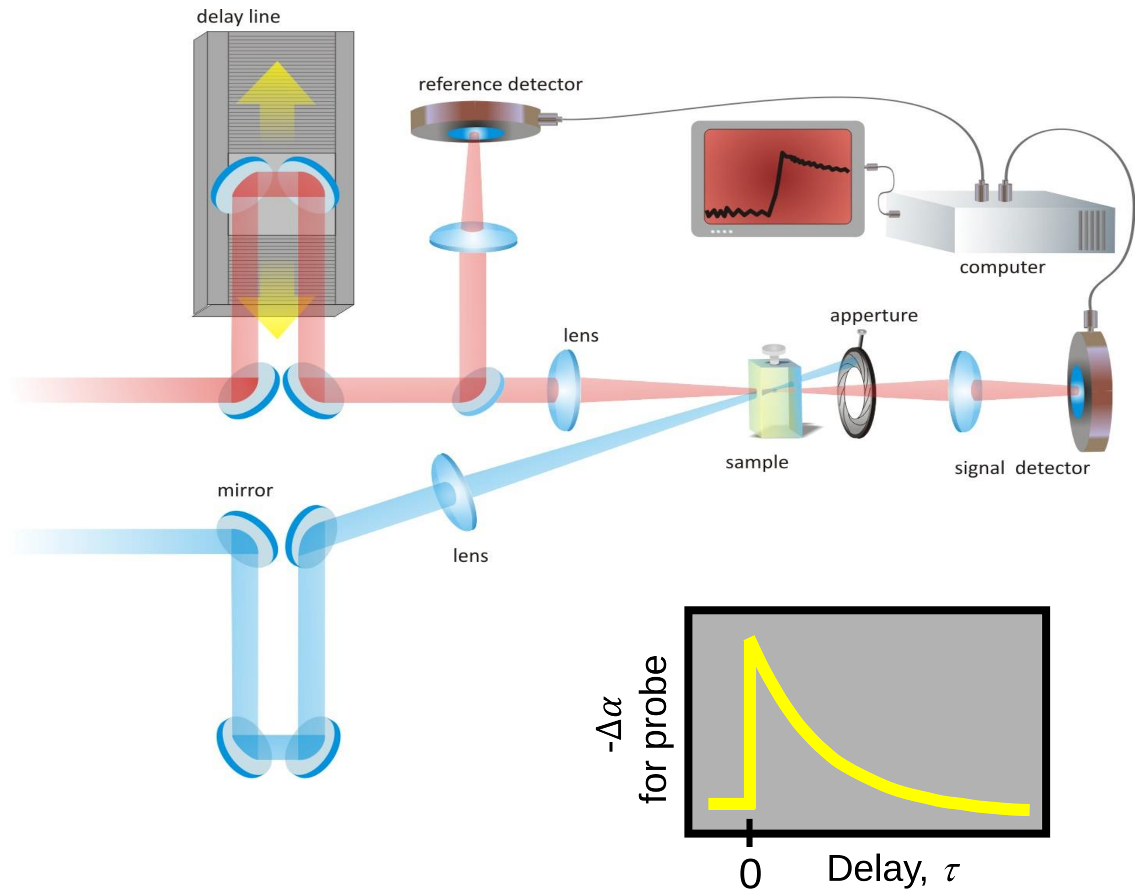
Pump pulse changes the population distribution and consequently,

Changes the absorption cross section
Changes the refractive index
Generates photoluminescence

Transient Absorption – Simplest Case

Change on the absorption cross section due to the presence of the pump beam.
Vary probe beam delay in a way that it will reach the sample before, together, and after the pump





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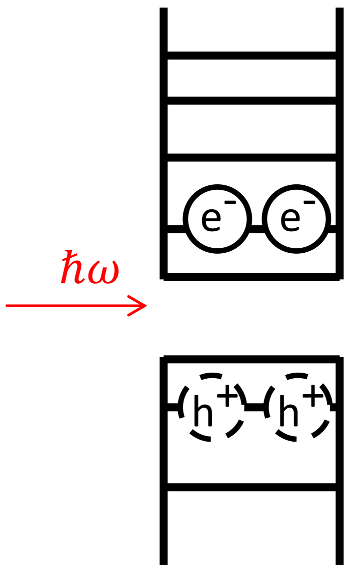

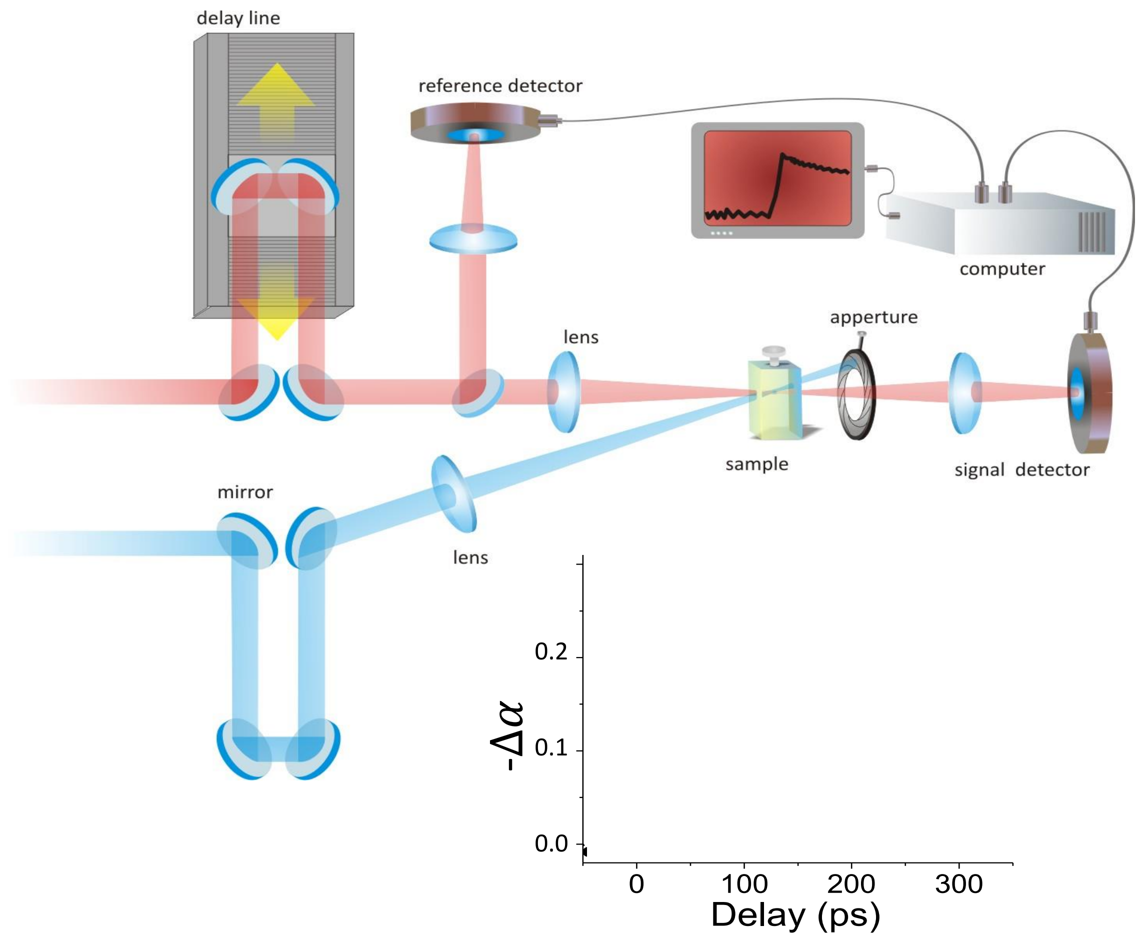

Transient Absorption – Modeling

Considering that, in the unexcited state, the medium have an absorption coefficient, α_0, which is decreased by $\Delta\alpha_0$ immediately after excitation. Assuming τ_{ex} is the excited-state lifetime, and that the excited states decay exponentially:

$$\Delta\alpha(\tau) = \Delta\alpha_0 e^{\left(-\frac{\tau}{\tau_{ex}}\right)} \qquad \text{for } \tau > 0$$

where τ is the delay after excitation.

So the transmitted probe-beam intensity—and hence pulse energy and average power—will depend on the delay, τ, and the lifetime, τ_{ex} (L = sample length):

$$I_{Trans}(\tau) = I_{Incident} e^{\left\{-\left[\alpha_0 - \Delta\alpha_0 e^{\left(-\frac{\tau}{\tau_{ex}}\right)}\right]L\right\}} = I_{Incident} e^{-\alpha_0 L} \ e^{\Delta\alpha_0 e^{\left(-\frac{\tau}{\tau_{ex}}\right)} L}$$

assuming $\Delta\alpha_0 L << 1$

$$I_{Trans}(\tau) \cong I_{Trans}(0^-) \left[1 + \Delta\alpha_0 e^{\left(-\frac{\tau}{\tau_{ex}}\right)} L\right]$$

The relative transmitted intensity is given by

$$\frac{\Delta T(\tau)}{T_0} = \frac{I_{Trans}(\tau) - I_{Trans}(0^-)}{I_{Trans}(0^-)} \cong \boxed{-\Delta\alpha_0 e^{\left(-\frac{\tau}{\tau_{ex}}\right)} L}$$

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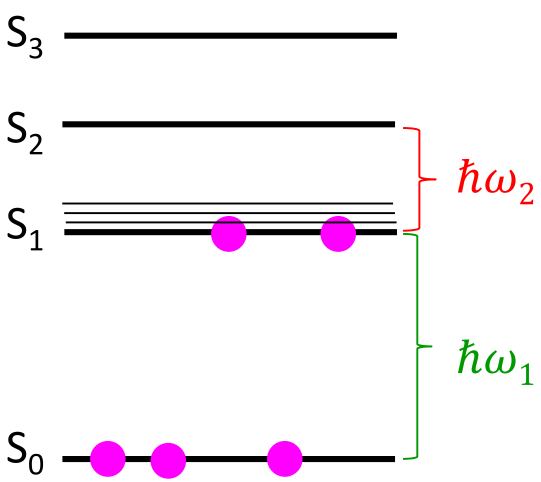
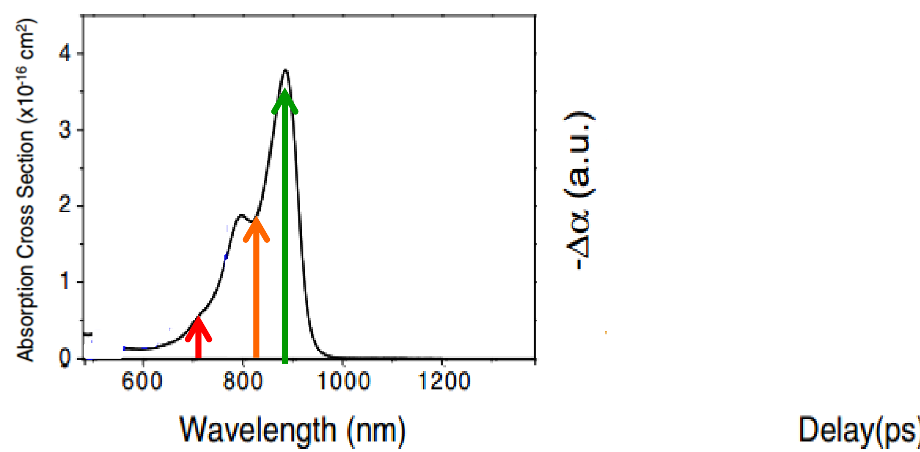
Transient Absorption – Modeling

$$\frac{\Delta T(\tau)}{T_0} = \frac{I_{Trans}(\tau) - I_{Trans}(0^-)}{I_{Trans}(0^-)} \cong -\Delta\alpha_0 e^{\left(-\frac{\tau}{\tau_{ex}}\right)} L$$

$\Delta T(\tau) > 0$ indicates decreasing in absorption, $\Delta\alpha_0 < 0$

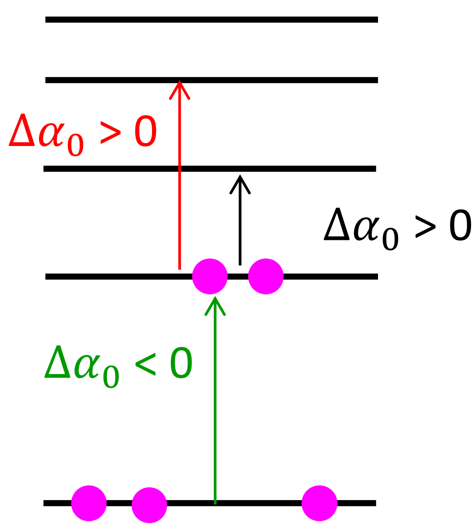
$\Delta T(\tau) < 0$ indicates increasing in absorption, $\Delta\alpha_0 > 0$



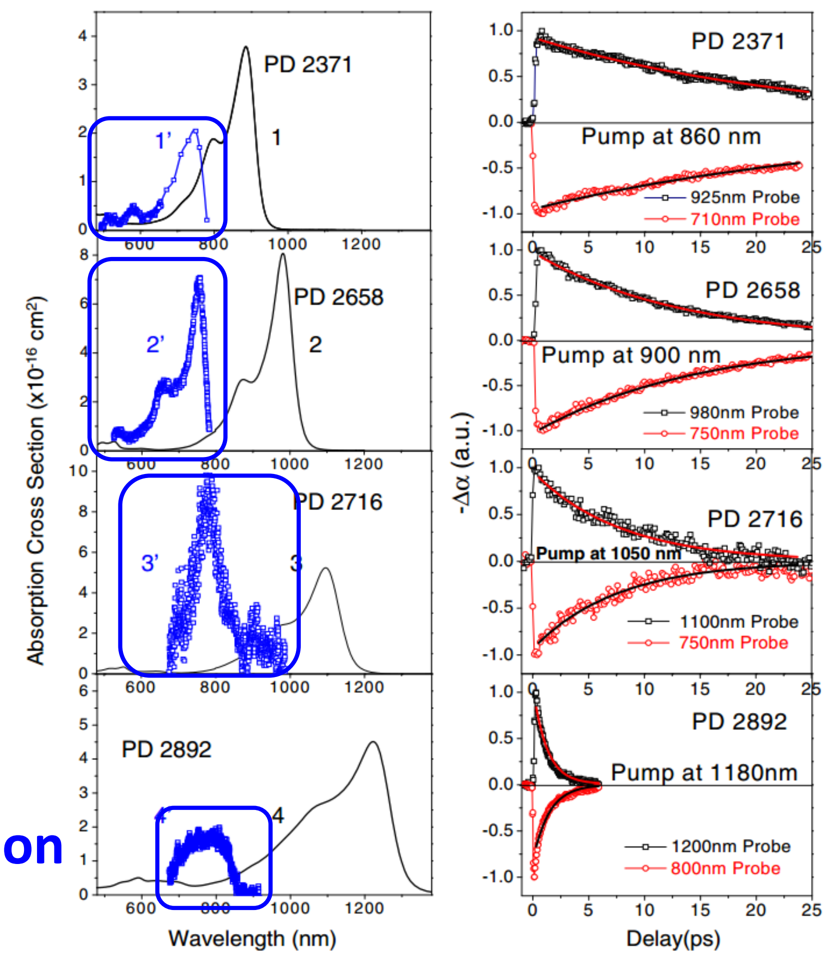


Why Spectroscopy?

Using **different pump** and/or **probe** photon **energies**, we can make a full picture of the charge/energy dynamics



Fix pump – WLC probe



ESA – Excited State Absorption

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Why Not Only One Wavelength?

800 nm – typical wavelength for Ti:sapphire amplifiers

Lets measure only at 800 nm!

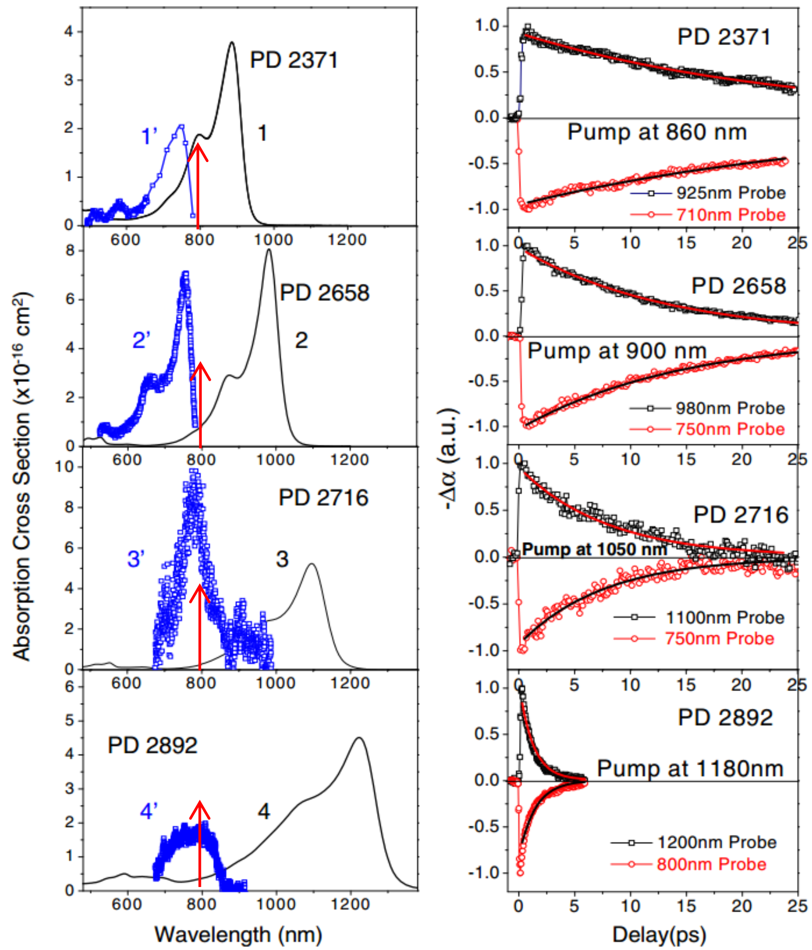
Which sample has larger ESA cross-section????

$$\sigma_{PD2371} = 0 \times 10^{-16} cm^2$$
$$\sigma_{PD2658} = 1 \times 10^{-16} cm^2$$
$$\sigma_{PD2716} = 4 \times 10^{-16} cm^2$$
$$\sigma_{PD2892} = 2 \times 10^{-16} cm^2$$

$\sigma_{PD2371} < \sigma_{PD2658} < \sigma_{PD2892} < \sigma_{PD28716}$

$\boldsymbol{\sigma_{PD2371} < \sigma_{PD2892} < \sigma_{PD2658} < \sigma_{PD28716}}$

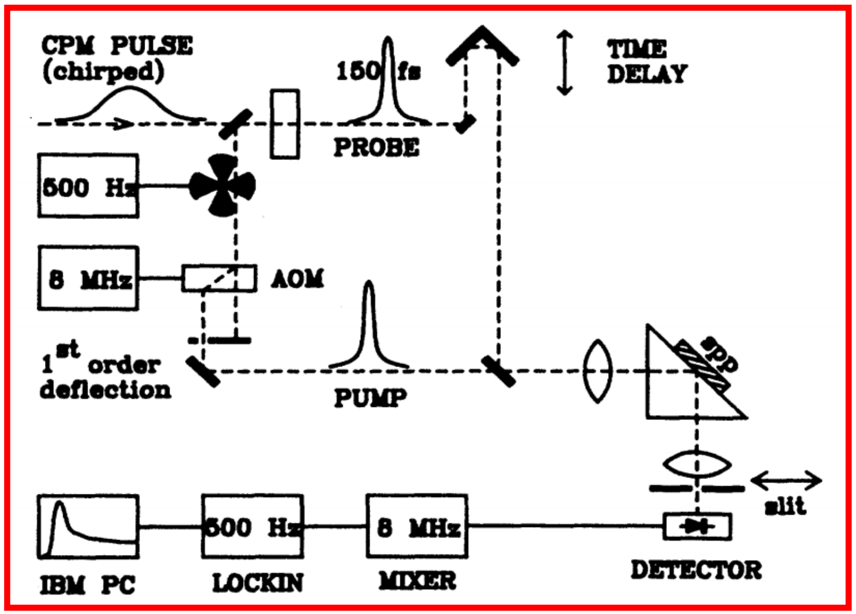
Fix pump – WLC probe

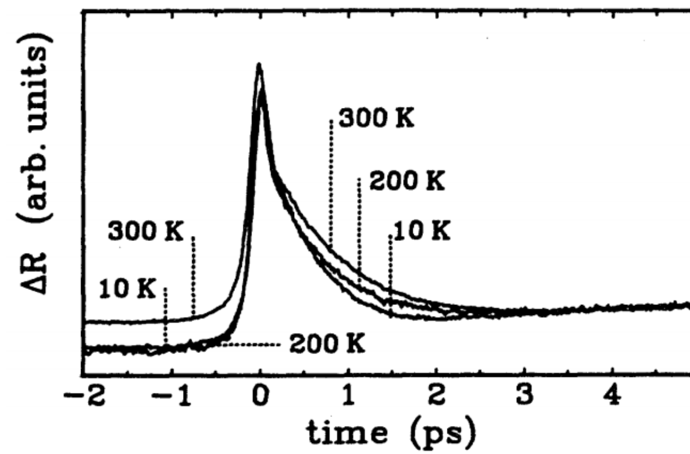


What if the Material is Not Transparent?

The answer is **pump-probe reflection spectroscopy**…

Measures changes in reflection due to the change on the population distribution
Also very useful to study surface spectroscopy



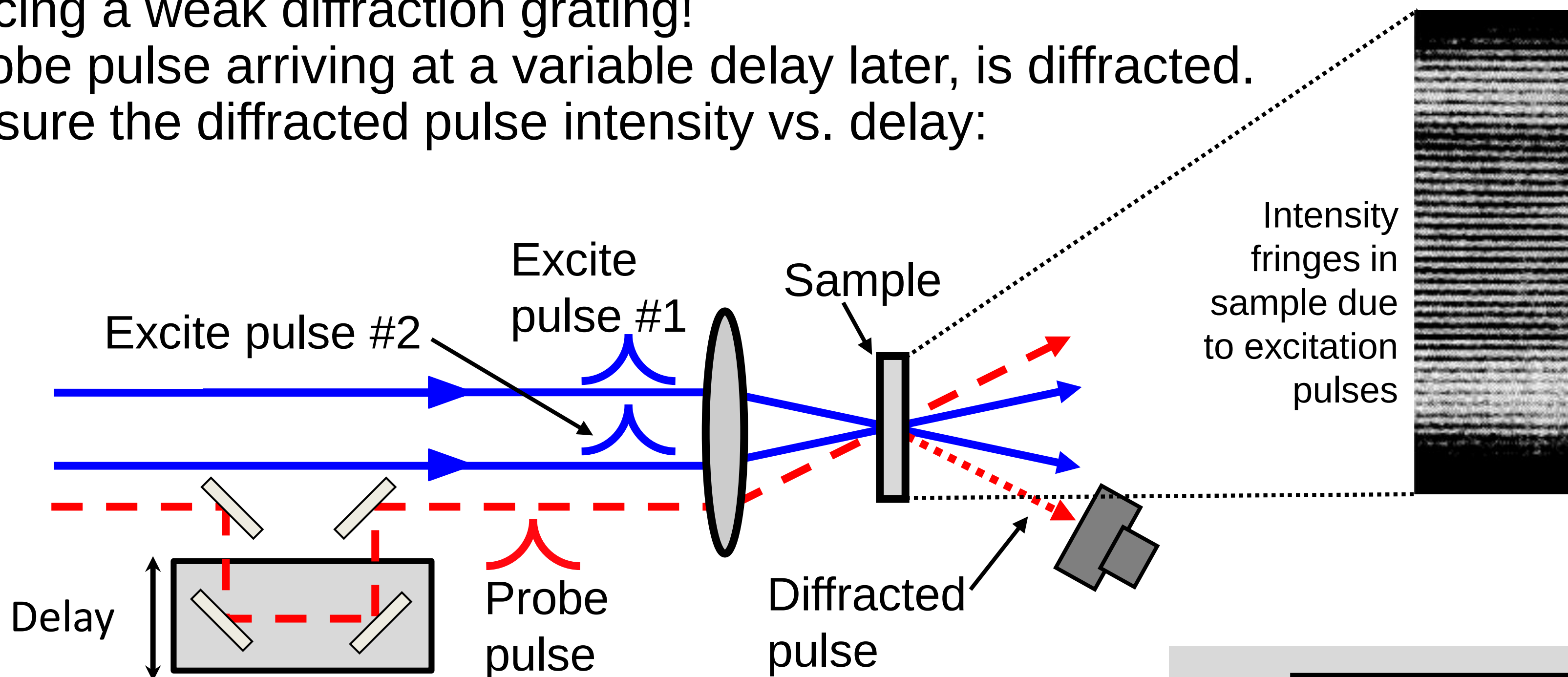


Example: Transient reflection of Ag films measured at different sample temperature showing that *e-ph* interaction gets faster at lower temperature
M. Groeneveld et.al. PRB 1995

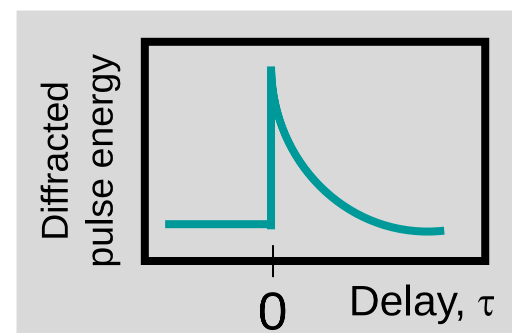
Similar setup – instead of collecting the transmitted beam, we collect the reflect one!

Transient-Grating Technique

Two identical pulses excite the sample simultaneously, inducing a weak diffraction grating!
A probe pulse arriving at a variable delay later, is diffracted.
Measure the diffracted pulse intensity vs. delay:



This is a **background-free** method, however the diffracted pulse intensity goes as the square of the diffracted field and hence is weaker than that in excite-probe measurements.



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Transient-Grating Technique

It measures changes in the absorption and refraction. The result is **the Pythagorean sum of the changes in the absorption *and* refractive index**. The diffraction efficiency, $\eta(\tau)$, is given by:

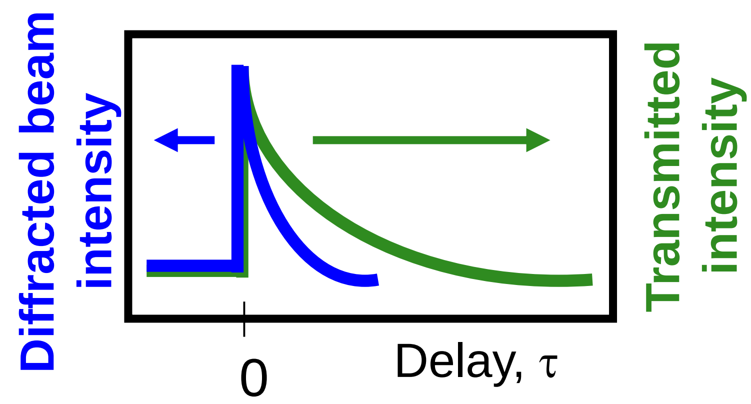
$$\eta(\tau) \approx [\Delta\alpha(\tau)L/4]^2 + [\Delta n(\tau)kL/2]^2$$

Absorption (amplitude) grating

Refractive index (phase) grating

This is in contrast to the excite-probe technique, which is only sensitive to the change in absorption and depends on it linearly.

If the absorption grating dominates and the excite-probe decay is exp($-\tau/\tau_{ex}$), then the TG decay will be exp($-2\tau/\tau_{ex}$):



H. Eichler, *Laser-Induced Dynamic Gratings*, Springer-Verlag, 1986.

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Transient Photoluminescence

Exciting a sample with an ultrashort pulse and then observing the **fluorescence vs. time** also yields sample dynamics.

Advantage:

Background free experiment – you measure PL intensity not ΔT!

You are able to distinguish from different species – two species might absorb at the same wavelength but might not emit at the same wavelength.

PL quenching indicates energy/charge transfer

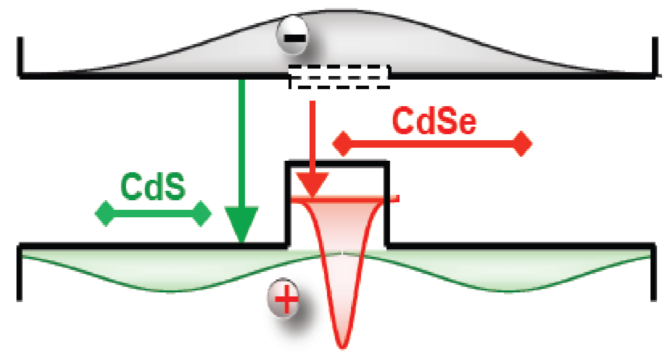
$$\boxed{1/\tau_{ex} = 1/\tau_{PL} + 1/\tau_{nr}}$$

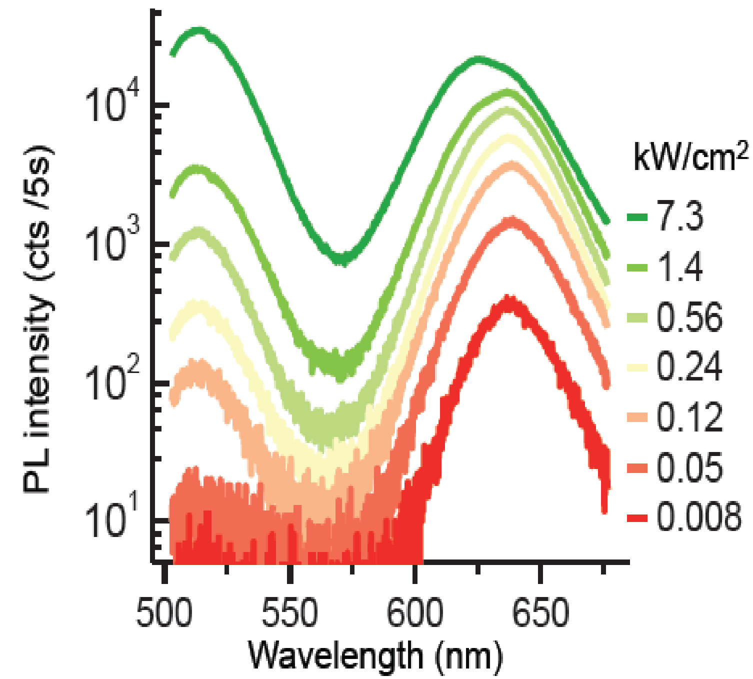
Disadvantage:

But how can we monitor the PL time evolution?

Experimentally more difficult to setup

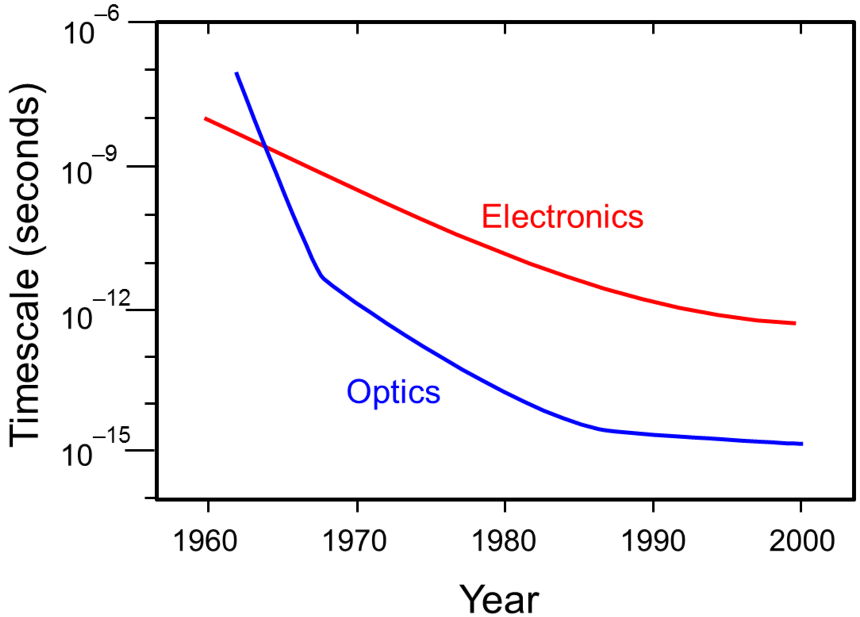
Sample has to have relatively strong QY





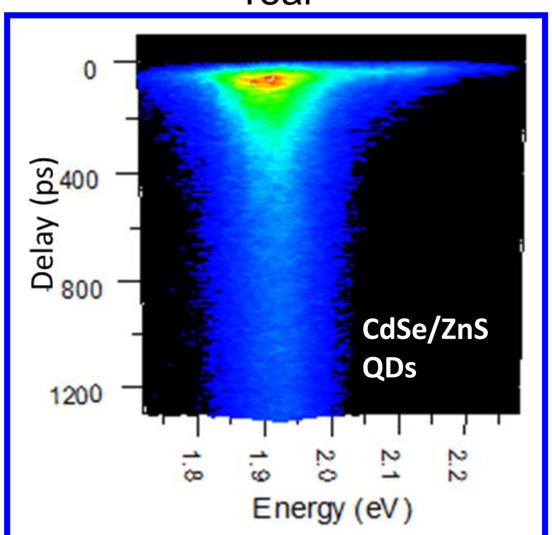
Galand et.al. Nano Lett. 2013

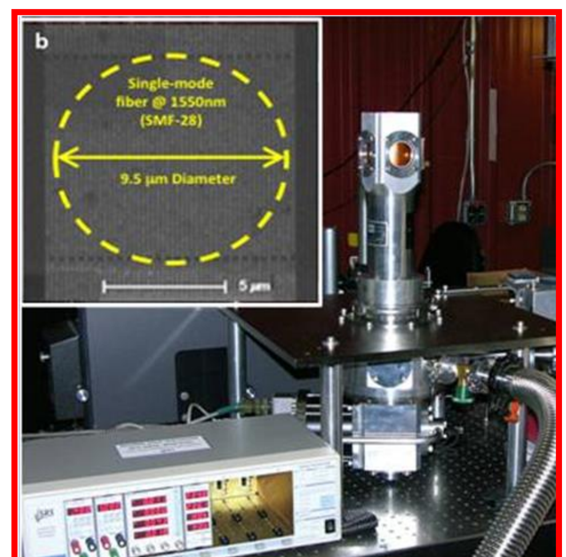
Transient Photoluminescence



If the process is slower than 10´s of picoseconds and emission is in the visible/NIR, TCSPC (~50 ps) and Streak Cameras (~10 ps) can take care of it!

For NIR (< 2.0 μm), novel superconductor nanowires single photon detectors (**SNSPD**) can respond as fast as 30 ps.





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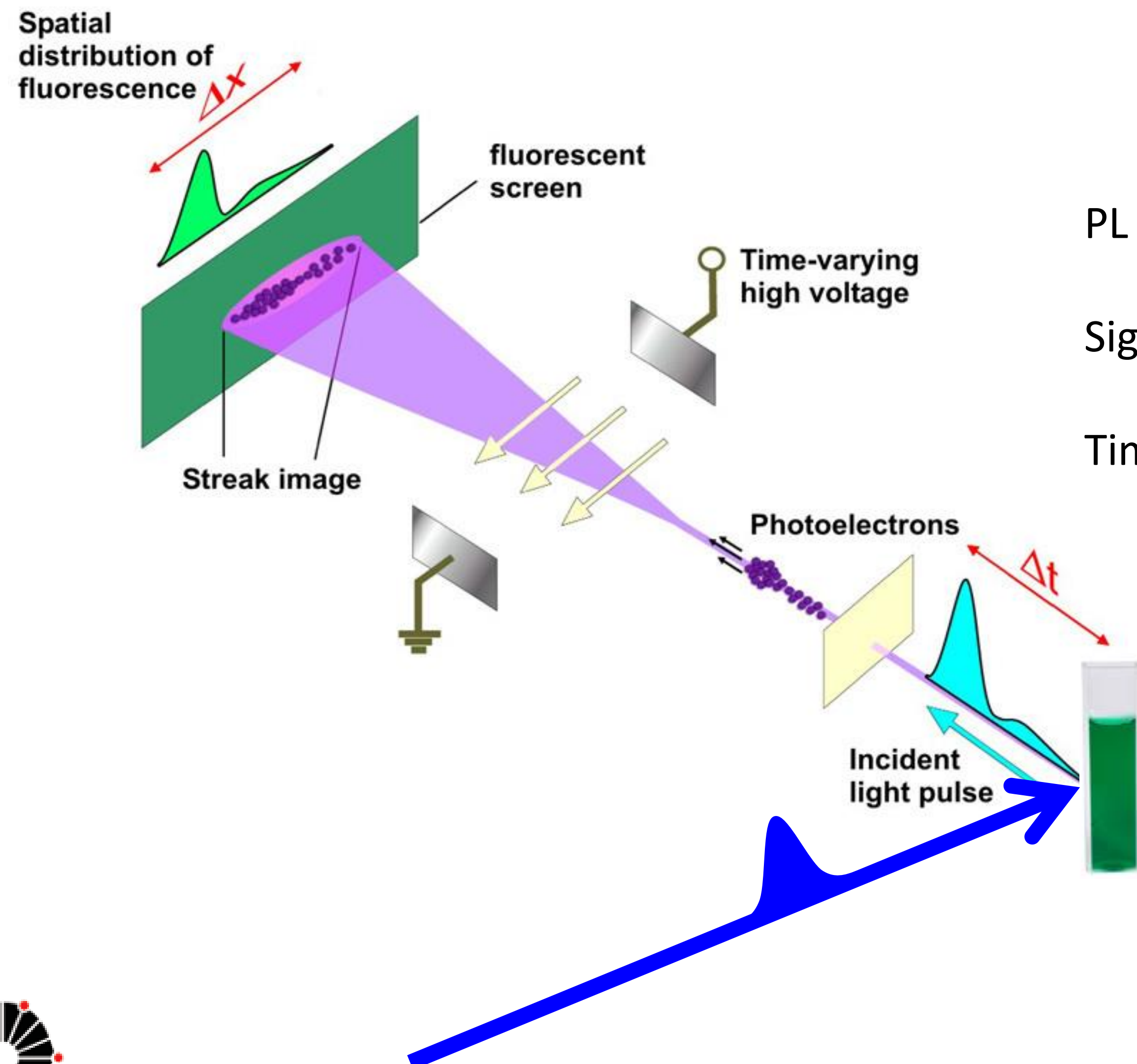
Visible Emission and Lifetimes Over 10’s Picoseconds

Life is easy – you can use a Streak Camera



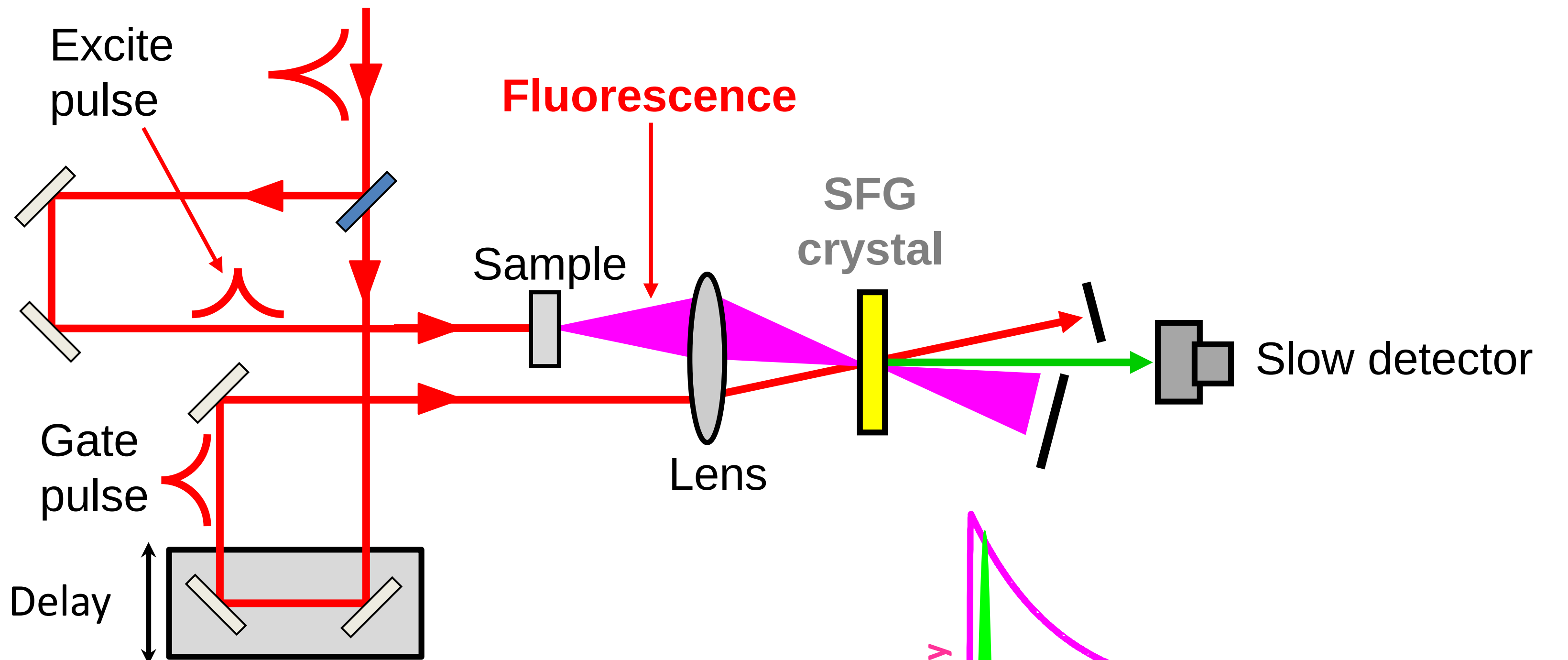
PL is collected through a spectrometer

Signal goes to the streak camera

Time varying HV spread the PL in time

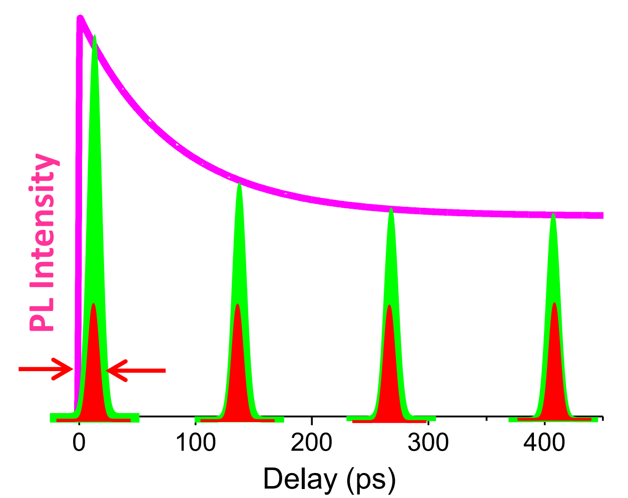
Transient Photoluminescence - uPL

If the dynamics is even faster (usually, due to non-radiative processes), PL is monitored by time-gating it with a probe pulse in a SFG crystal.



Time resolution given by the gate pulse

Intensity given by PL



Transient Photoluminescence - uPL

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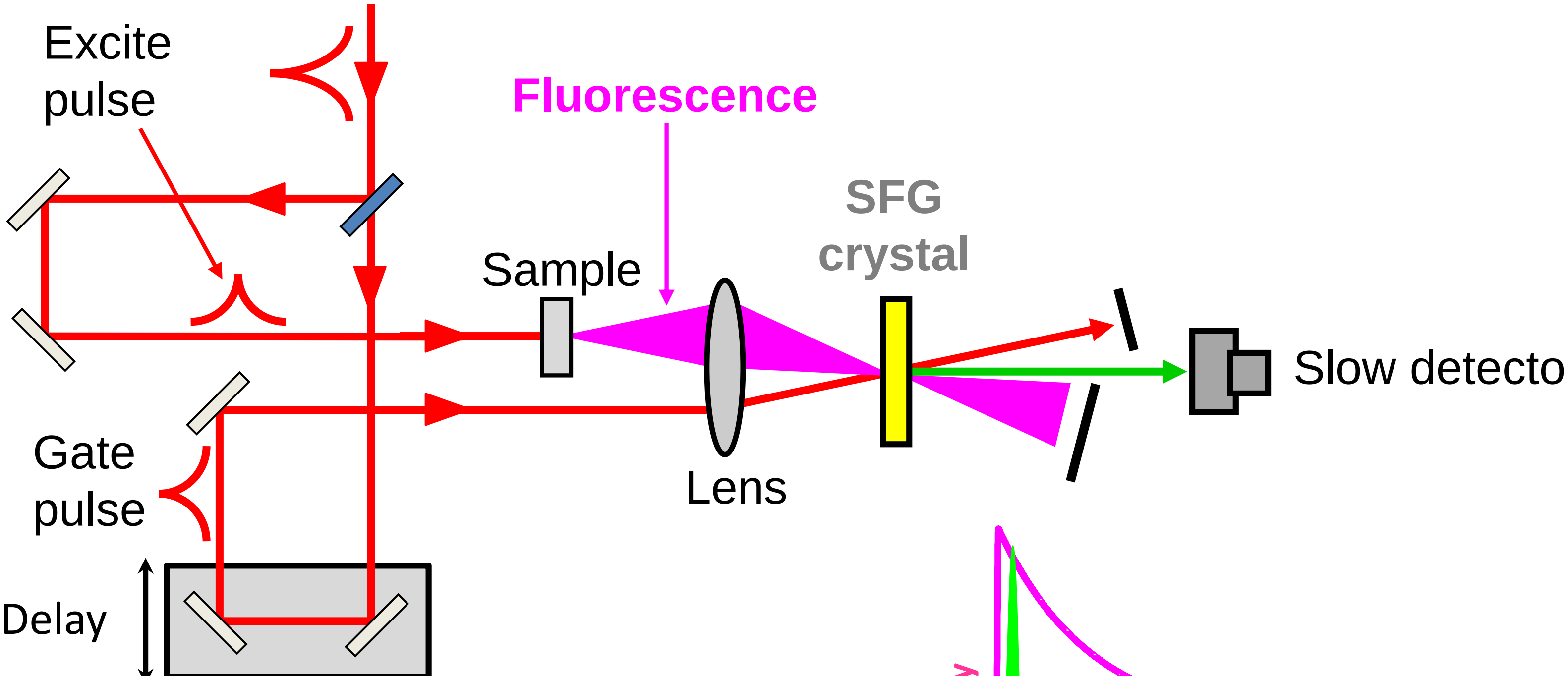

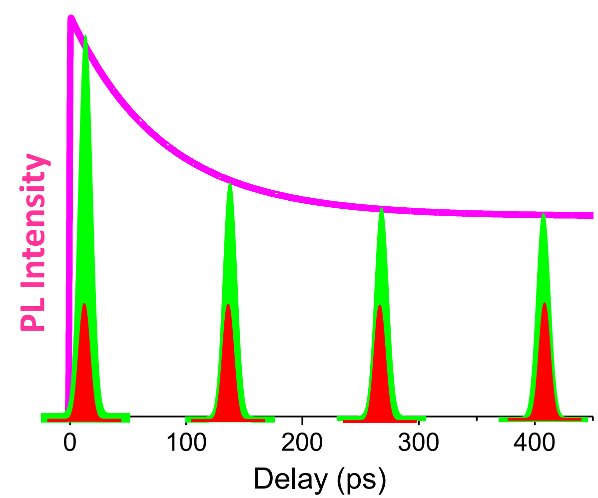

Why is this difficult???

Low PL collection efficiency

Low SFG efficiency

Phase matching

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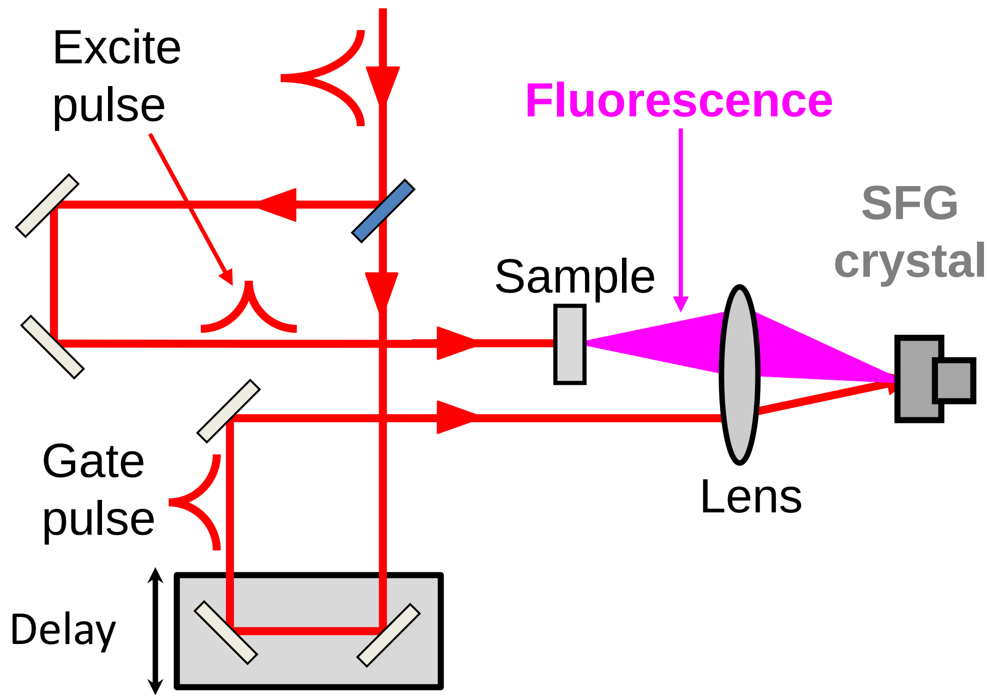
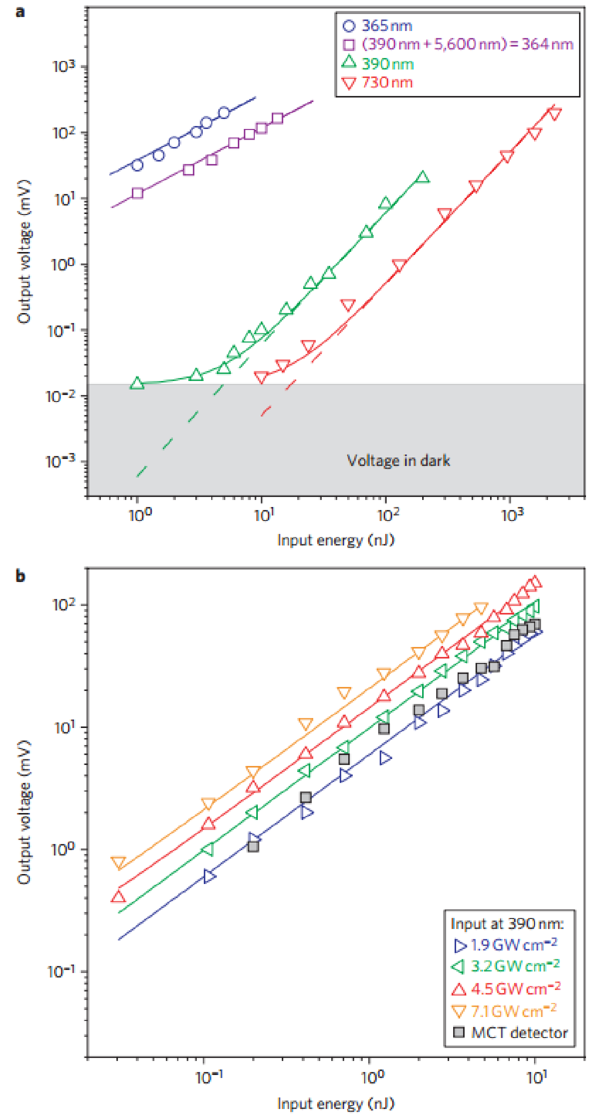
Transient Photoluminescence – Alternative Way

In principle, instead of using a SFG crystal, do direct two-photon absorption in the detector.





5.6 μm detected with GaN PD

Fishman et.al., Nat. Photon. 2011

Do not require phase matching
Still background free
However, it has never been tested

Take-home message

To measure something fast you need a even faster “stopwatch”

Changing excitation and probe wavelengths is fundamental for a complete picture of the physical phenomena

Using ultrashort pulses and delay stages we monitor the changing dynamics in absorption, refraction, emission, polarization, etc.

The most appropriated technique depends on the sample to be studied and the question to be answered.

More complexes experiments allows for measurements of coherent evolution of the population distribution – dephasing times and homogeneous broadening

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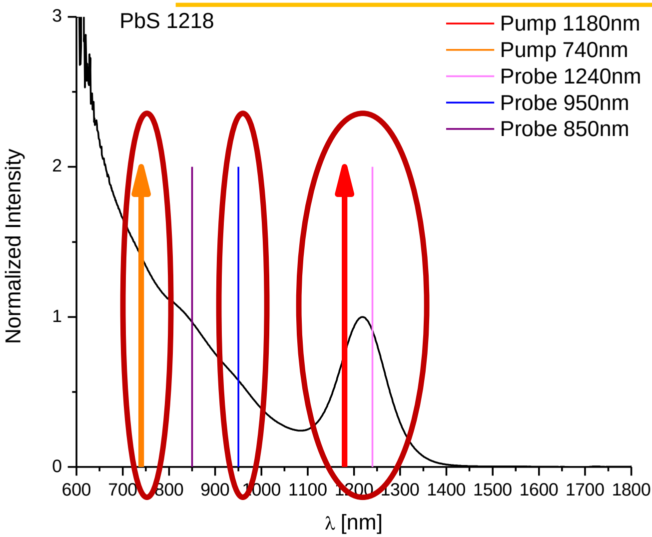
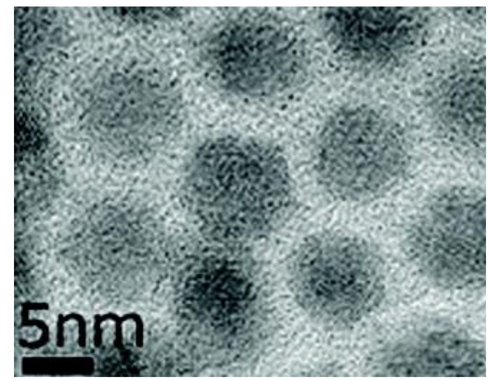
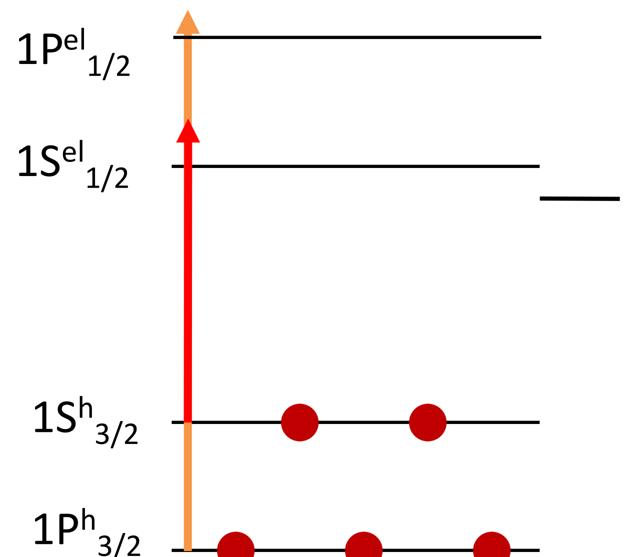
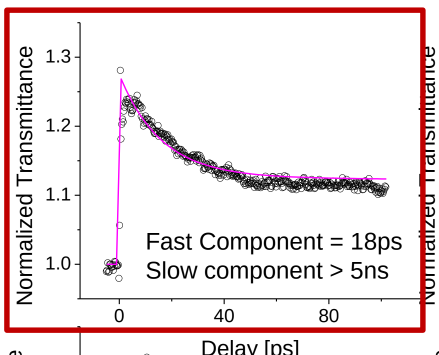
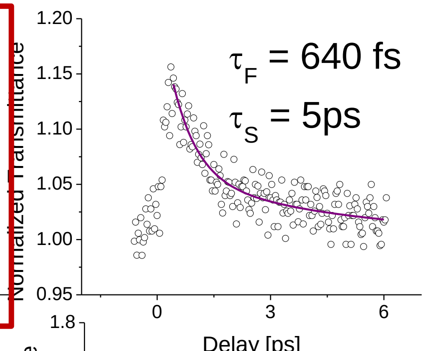
Carrier Dynamics in PbS Quantum Dots

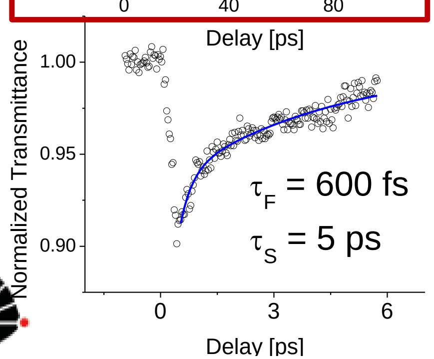


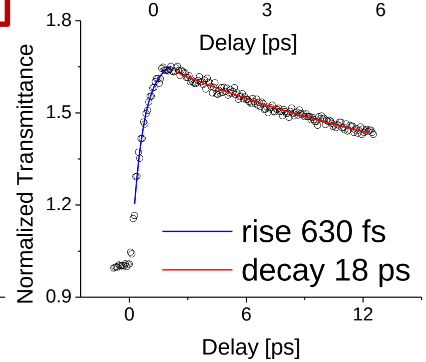




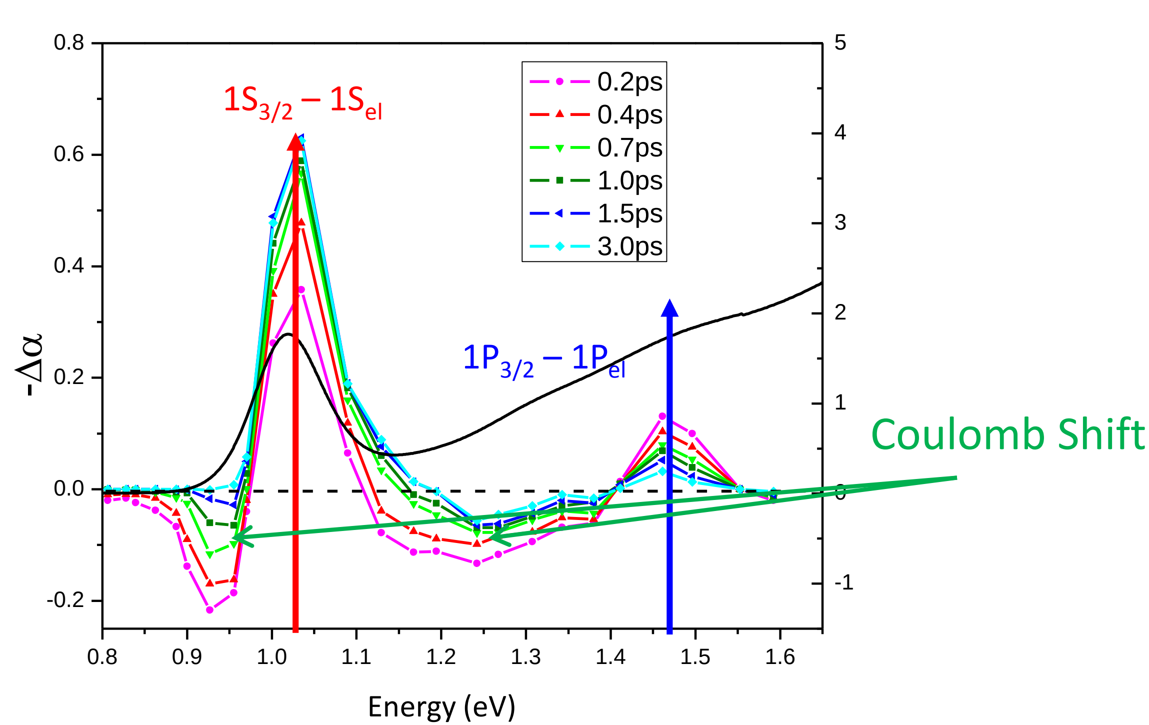


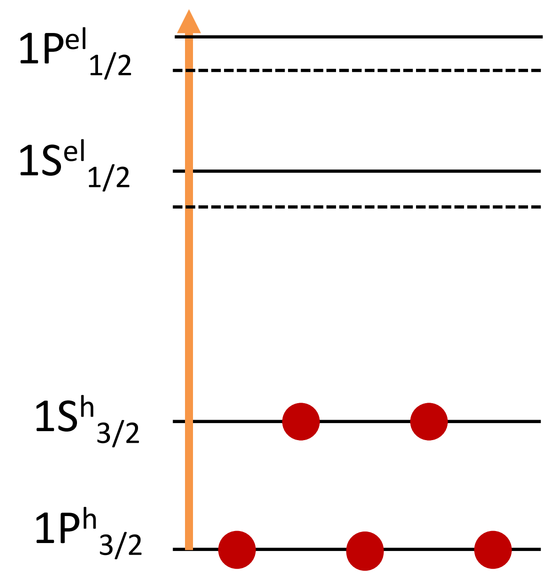






Carrier Dynamics in PbS Quantum Dots





1. Electrons rapidly populates 1P level
2. Slowly, they decay to the 1S level
3. Exciton-exciton interaction generates Coulomb shift which decreases effective energy level

We can only understand the entire dynamics because we used multiple probe wavelengths

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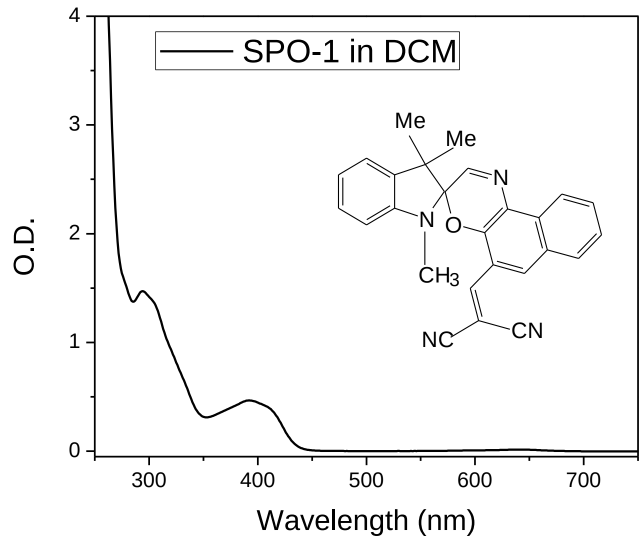
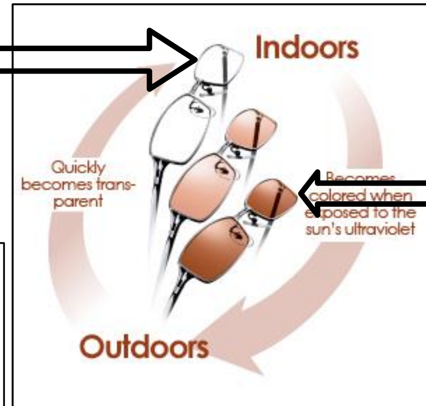
Photochromic Materials – Chain Opening Dynamics

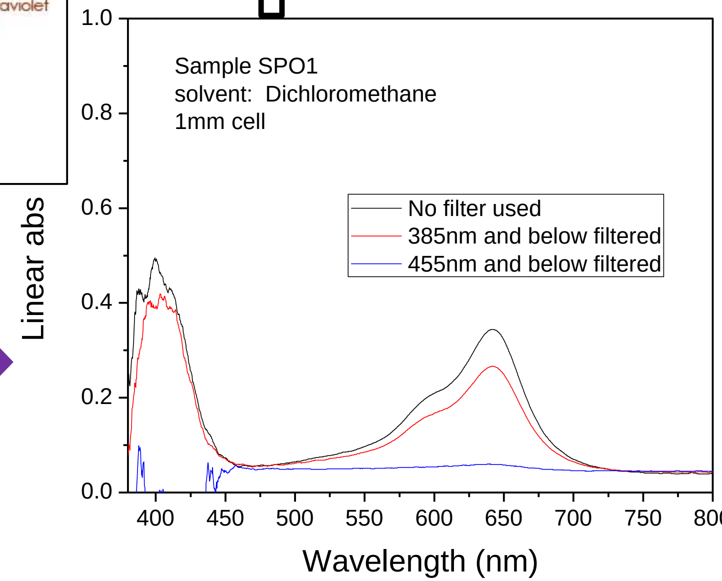
Closed Form





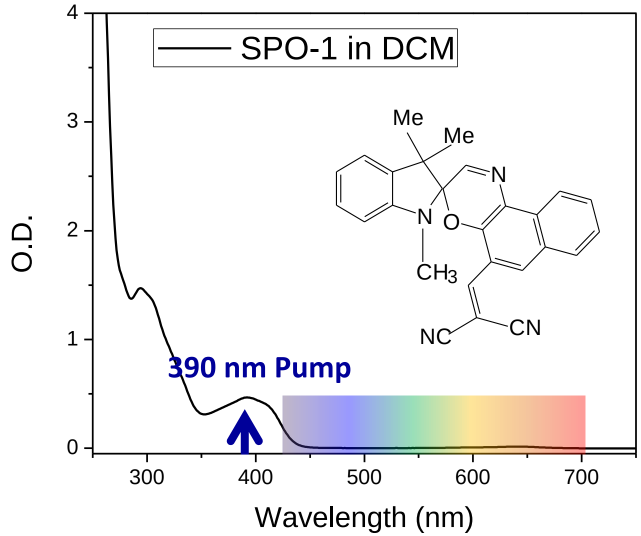
UV

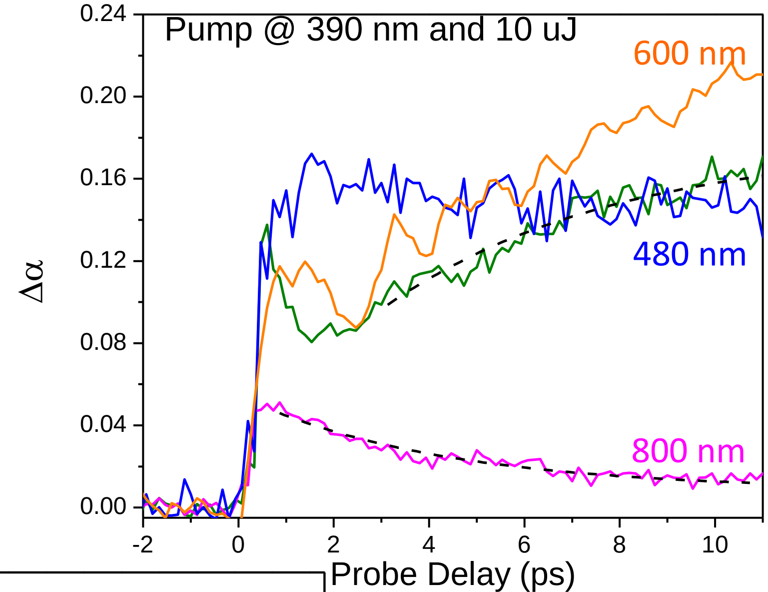
Open Form

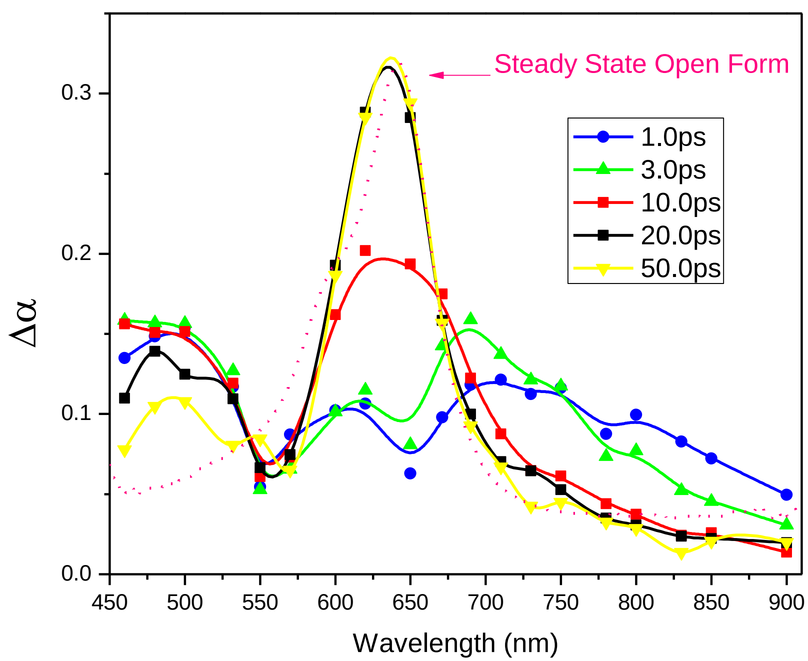


How can we understand the dynamics of the molecular structure change???

Photochromic Materials – Chain Opening Dynamics







- ✓ Right after being excited, 1 ps, a broad band absorption is formed due to intermediate forms of the molecule.
- ✓ After about 3 ps the main peak starts to take form and the NIR absorption started to vanish.
- ✓ The complete “open form” is achieved at ~ 20 ps after the excitation, the main peak is formed and agrees very well with the steady state measured with continuum UV excitation.

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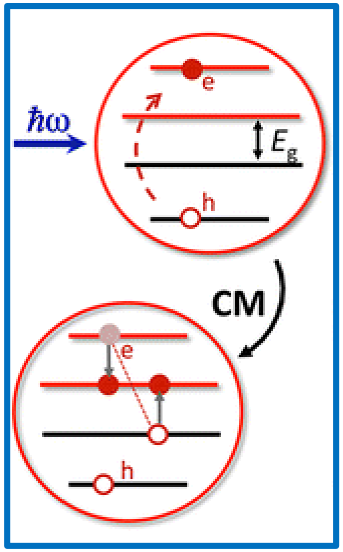
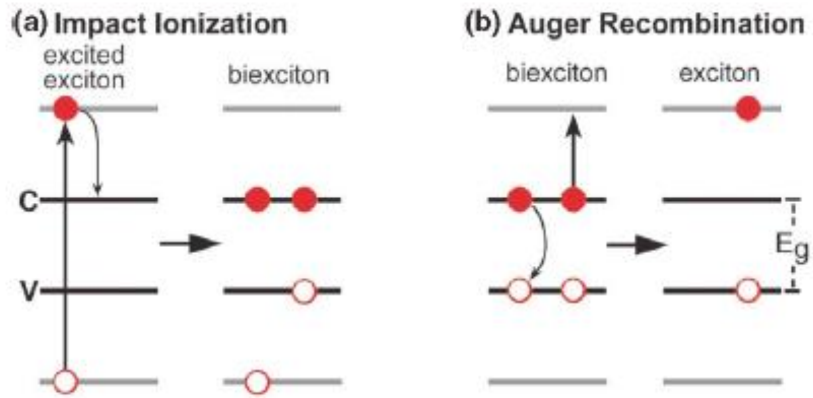
Using uPL to Study Carrier Multiplication in QDs



Padilha et al., Acc. Chem. Res.(2013)

CM – A high energy photon can create more than one low energy electron-hole pair (exciton)



CM could boosts **photovoltaic efficiency** for more than **30%**

For a very **low excitation intensity**, a **biexciton** is present only if this is created **via CM**

Using uPL, we can look for biexciton signature (Auger decay) to identify CM and its efficiency

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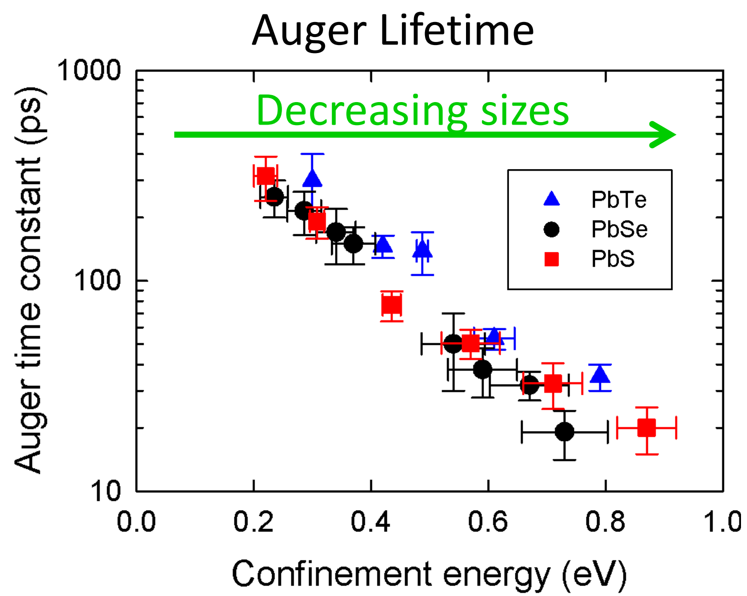
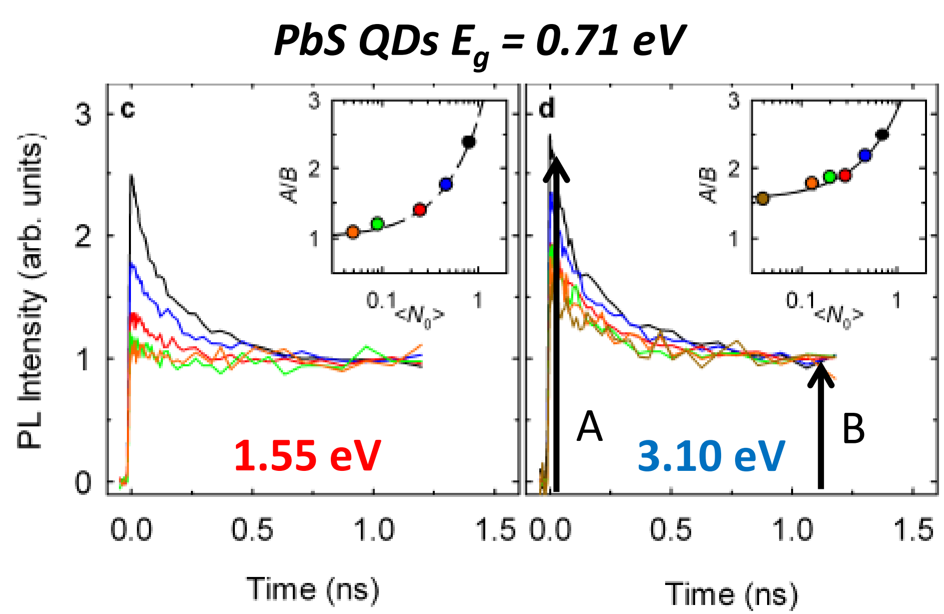
Using uPL to Study Carrier Multiplication in QDs



Auger time constants are well know for PbS QDs.

In this case, we vary the pump wavelength to look for low intensity biexcitons



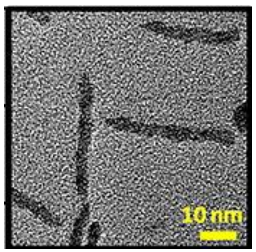
When CM is not present, early times dynamics due to biexcitons follows Poisson Statistics

When CM is present, even for <N> << 1, biexcitons are present

Using UFS to boost Carrier Multiplication in QDs

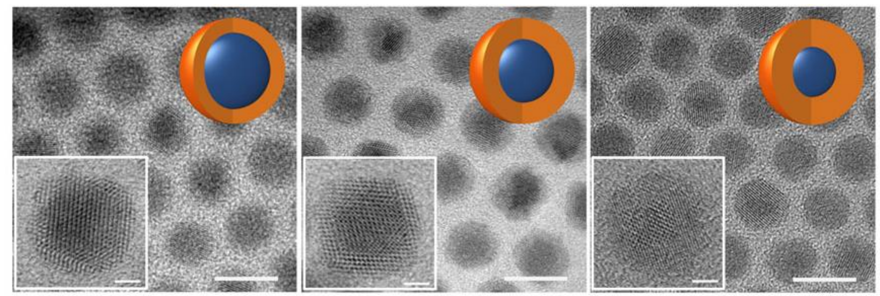
Based on the UFS results for QDs, we have developed new materials for enhanced CM

PbSe Nanorods

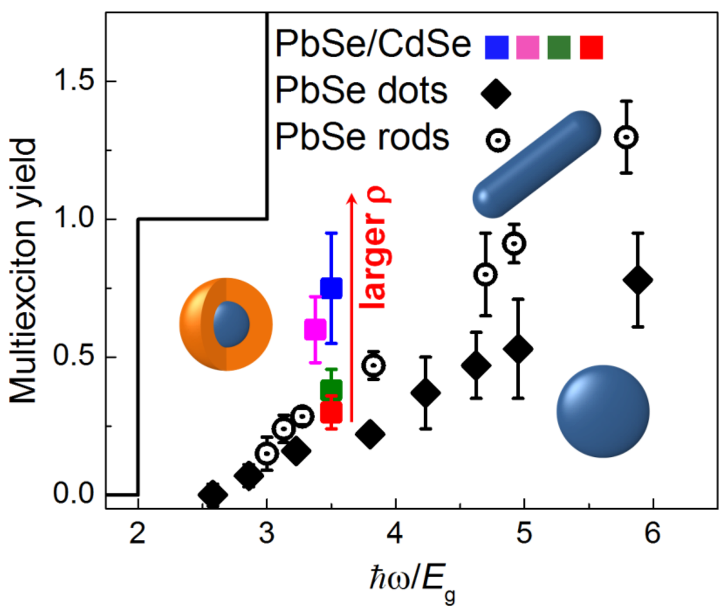


Padilha et.al. Nano Lett. 2013

PbSe/CdSe Quase-Type II



Cirloganu et.al. Nat. Comm. 2014

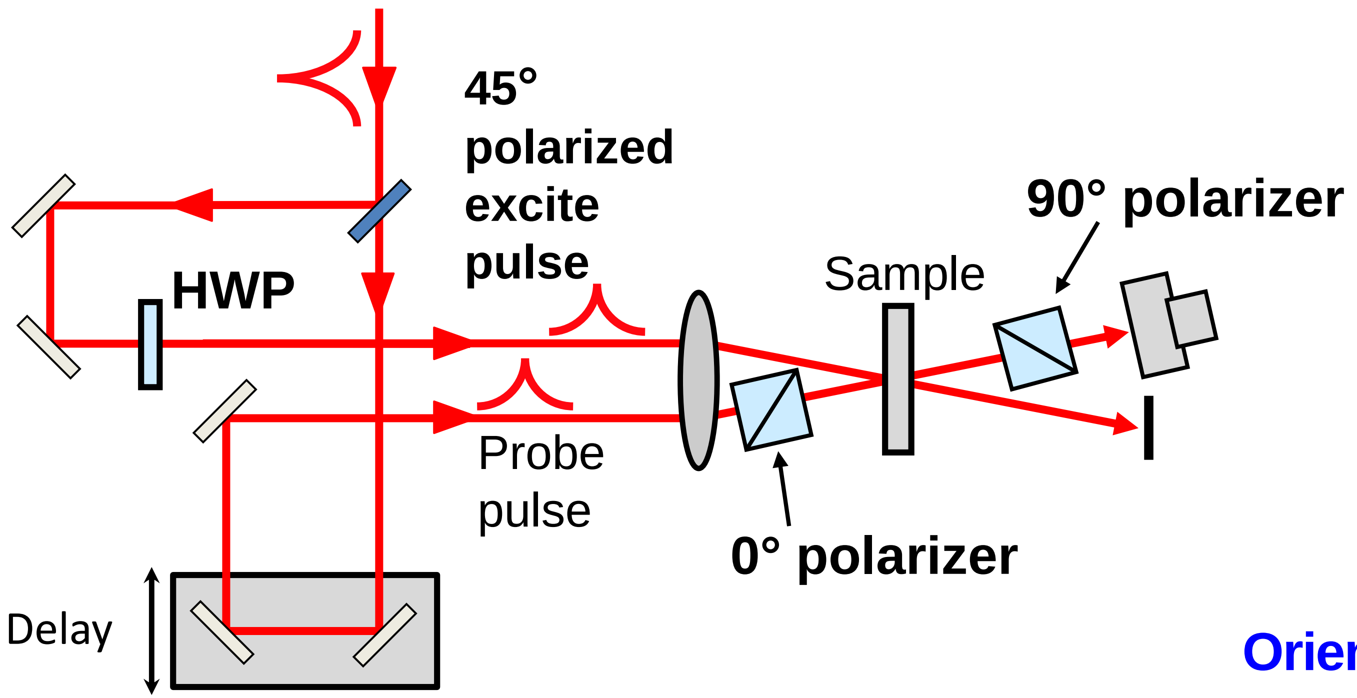


From QDs to Quase-type II core/shell we have an 4-fold enhancement on CM efficiency

Promising results towards Generation –III solar cells.

Other Techniques

Ultrafast Polarization Spectroscopy



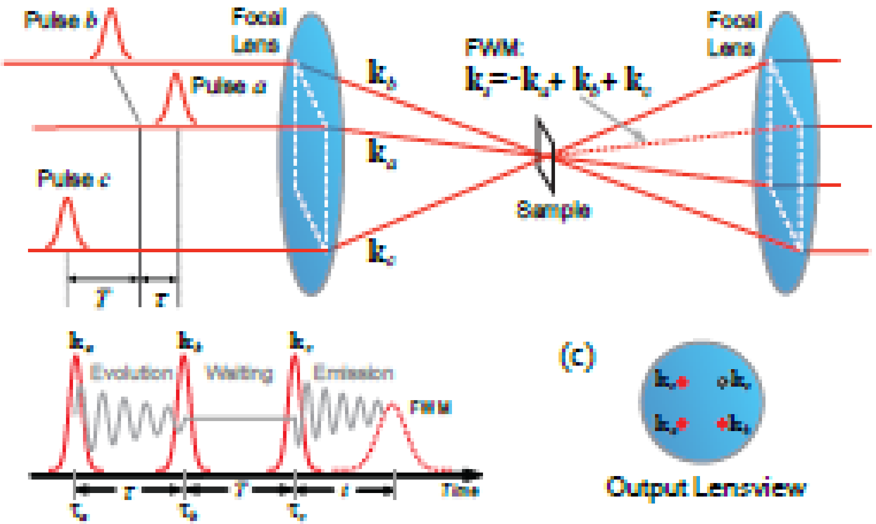
Induced dichroism

Orientational relaxation

Birefringence

Other Techniques

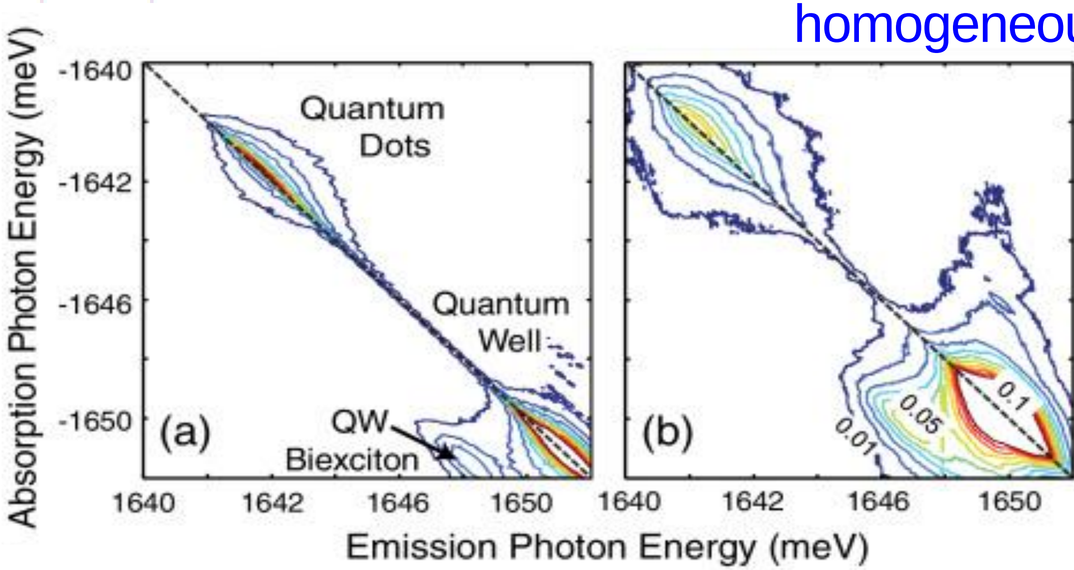
Multidimentional Fourier Transform Spectroscopy



Heterodyne detection of the FWM signal as a function of different time delays.

Take the Fourier Transform to go to the frequency domain

Measures dephasing times – homogeneous linewidth



Remember Cundiff’s talk

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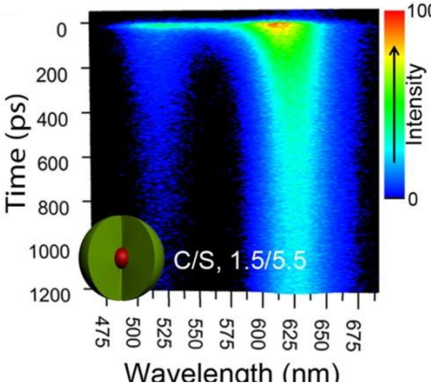
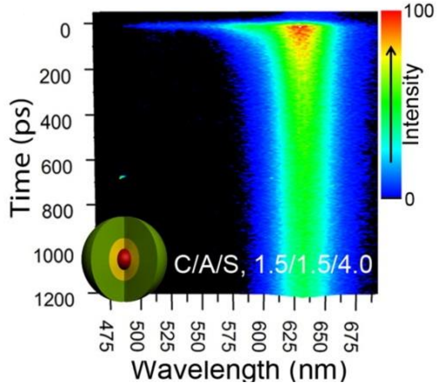
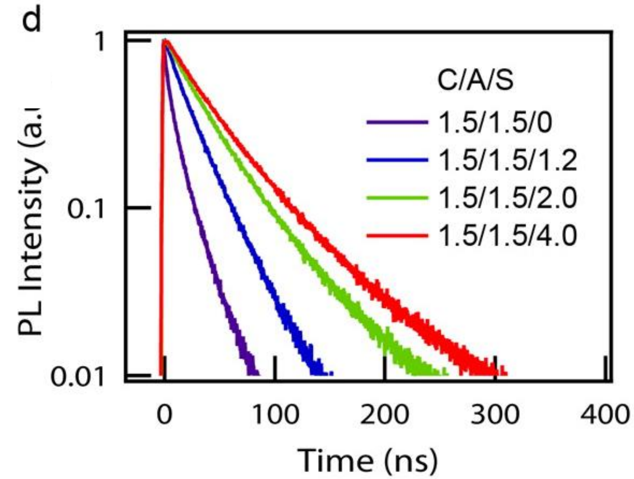
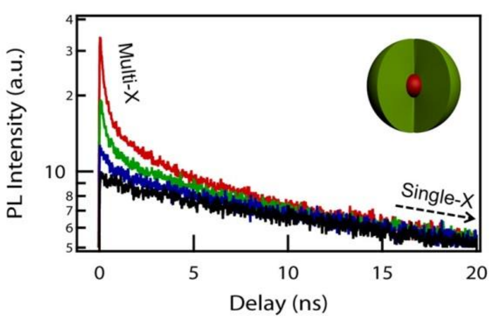
Transient Photoluminescence – QDs based LEDs

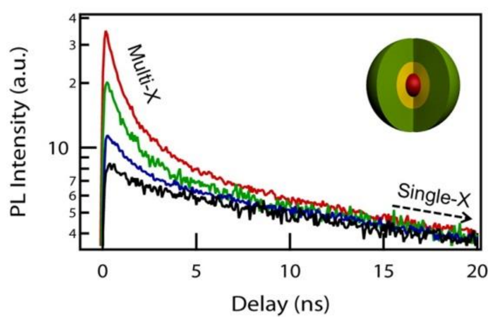
Dual emission from Core/Shell QDs



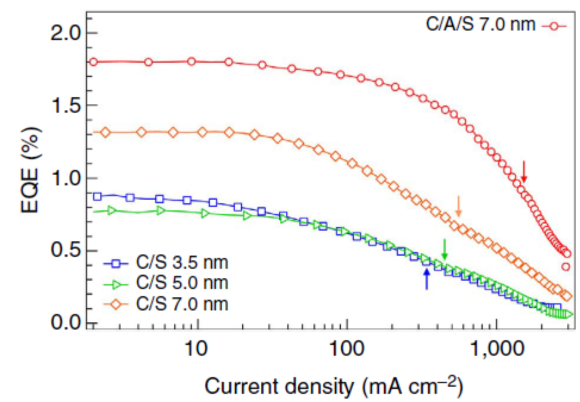


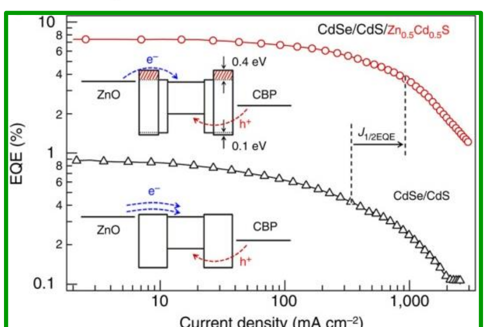


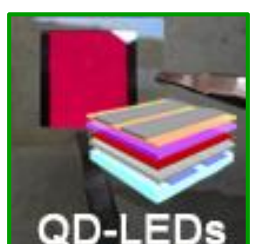




Less non-radiative losses results in more efficient LED´s







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