"Leading edge experimental techniques":

Ultra fast optical spectroscopy

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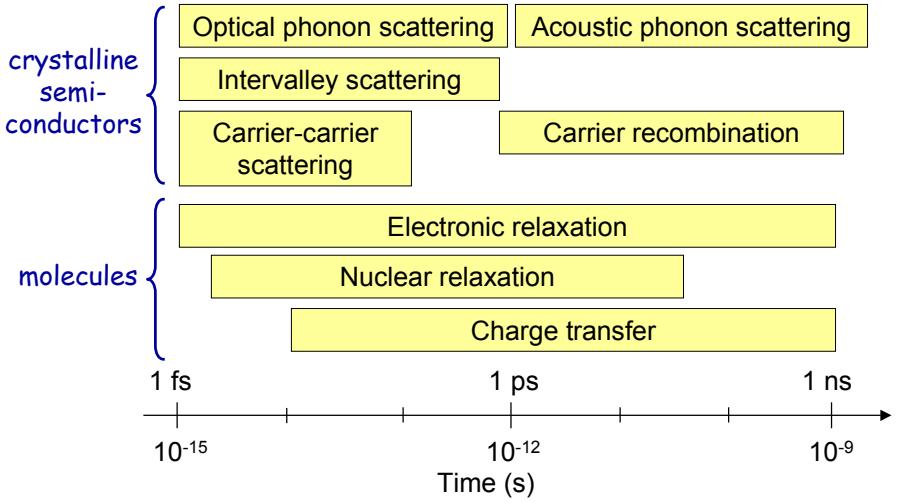
Ultra fast optical spectroscopy

Outline

1. Introduction
2. Generation of ultra short laser pulses
   i. Mode-locking
      - The principle
      - Active/passive techniques
   ii. Pulse characterization
3. Ultra fast spectroscopic techniques
   i. PL up-conversion
   ii. PL X-correlation
   iii. Transient absorption/reflection
   iv. Transient grating techniques
4. Not-quite-so-fast techniques

Why ultra fast?
Relaxation processes in photoexcited matter:



Ultra fast optical spectroscopy

Definition of "ultra fast":

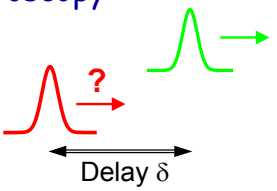
The term "ultra fast" currently implies a timescale of ≈ 10fs – 1ps.

Examples ofultra fast processes:

- cis-trans isomerization of rhodopsin ~ 60 fs (important step in vision)
- electron transfer in photosynthetic reaction centres: ~ 100 fs
- carrier thermalization in GaAs: ~ 100 fs

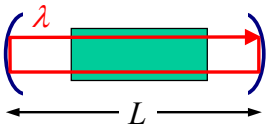
The general idea of ultra fast spectroscopy:

1. Trigger an event with one short laser pulse
2. Probe the dynamics of a process with a second pulse



Longitudinal modes in a laser cavity:

LASER = gain medium + resonator

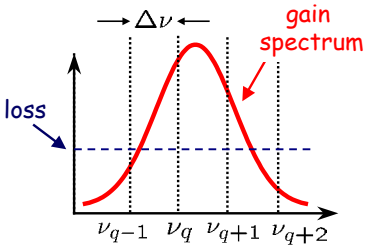


For a cavity mode to be sustained we need:

$$2L = q\lambda$$

⇒ Frequency spacing of longitudinal modes:

$$\begin{aligned}\Delta\nu &= \nu_{q+1} - \nu_q \\ &= \frac{c}{\lambda_{q+1}} - \frac{c}{\lambda_q} \\ &= \frac{c}{2L}\end{aligned}$$



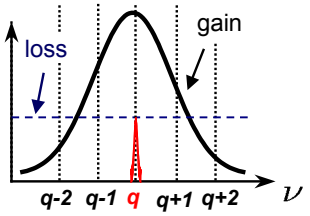
Ultra fast optical spectroscopy

Homogeneously broadened medium:

All cavity modes compete for the same gain medium.

After a while, only the mode with the strongest gain will oscillate.

⇒ Single-mode operation

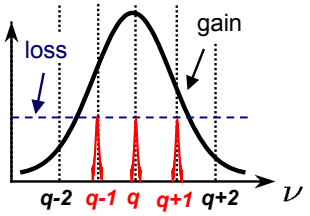


Inhomogeneously broadened medium:

Cavity modes compete for different components of the gain medium.

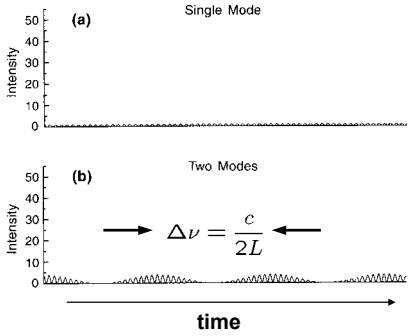
All modes for which the gain is larger than the losses can oscillate.

⇒ Multi-mode operation



Take a laser sustaining two longitudinal modes:

$$E_1 = \hat{E}\cos[\omega_q t + \varphi_q(t)]$$
$$E_2 = \hat{E}\cos[\omega_{q+1} t + \varphi_{q+1}(t)]$$



Output Intensity is the square of the sum:

$$I = (E_1 + E_2)^2$$
$$= 4\hat{E}^2 \sin^2\left[\left(\frac{\omega_{q+1}+\omega_q}{2}\right)t + \left(\frac{\varphi_{q+1}+\varphi_q}{2}\right)\right] \cos^2\left[\left(\frac{\omega_{q+1}-\omega_q}{2}\right)t + \left(\frac{\varphi_{q+1}-\varphi_q}{2}\right)\right]$$

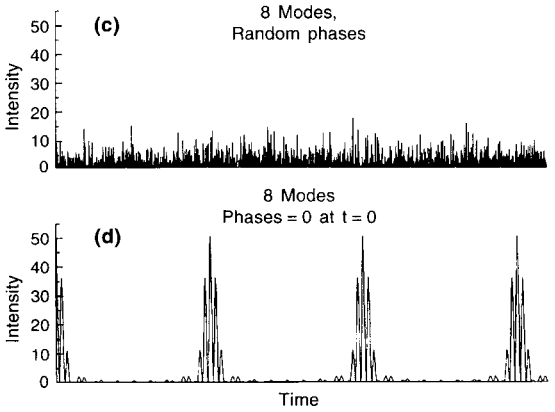
term varying at optical frequency ~10^{14} Hz

Envelope varying slowly with $\Delta\nu = c/2L$ *if the two phases are locked in time (i.e. non-random)*

Can we make a pulsed laser using this?

Answer: yes !

(If we can lock together the phases of many modes in time)



Lock together a Gaussian distribution of modes:

$$E(t) = \sum_{-\infty}^{+\infty} E_n \exp(i\omega_n t) \quad \text{with} \quad \omega_n = \omega_0 + n\Delta\omega$$

$$\text{and} \quad E_n = E_0 \exp\left[-\left(\frac{2n\Delta\omega}{\Delta\omega_0}\right)^2 \ln 2\right]$$

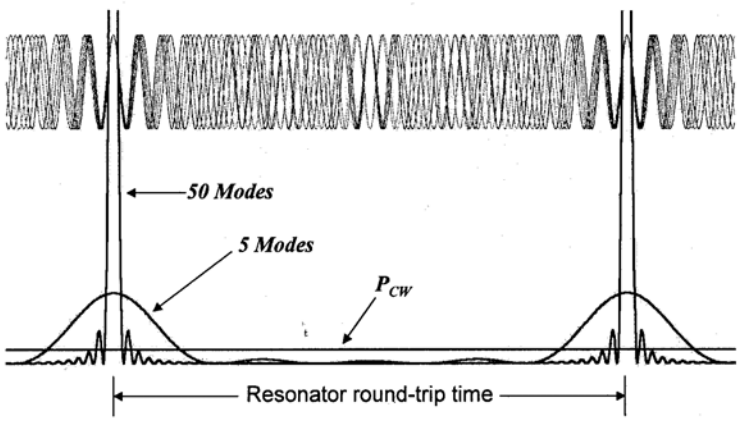
$$E(t) = \exp(i\omega_0 t) \underbrace{\sum_{-\infty}^{+\infty} E_n \exp(in\Delta\omega t)}$$

fourier transform of E_n

$\Rightarrow$ Intensity of laser output: $\langle I \rangle = \langle E(t)\, E^*(t) \rangle \propto exp\left[-\left(\frac{2t}{\tau_p}\right)^2 \ln 2\right]$

with pulse duration: $\tau_p = \frac{2\sqrt{2}}{\pi\, \Delta\omega_0} \ln 2$ $\Rightarrow$ pulses are the shorter, the broader the gain medium!

Ultra fast optical spectroscopy



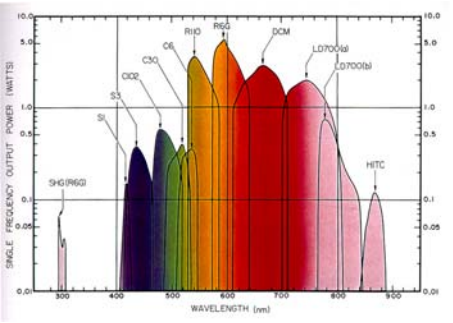
M. Didomenico, J. Appl. Phys. Lett. 35, 2870 (1964); L. Hargrove *et al.*, Appl. Phys. Lett 5, 4 (1964)

$\Rightarrow$ to generate ultra short pulses we need to use particularly broad gain media to lock together as many modes as possible

Examples for broad gain media:

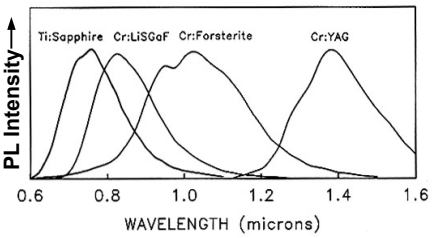
<u>Organic dyes:</u>

broad spectra caused by strong electron – phonon coupling in π-conjugated molecules



<u>Ion-doped crytals:</u>

solid-state, allowing high gains at low noise



Ultra fast optical spectroscopy

Mode-locking techniques

Idea: make cavity losses larger for continuous (CW) operation than for pulsed operation

Active mode-locking:

introduce cavity losses modulated at the frequency $\Delta\nu=c/2L$ (using e.g. an acousto-optic modulator)

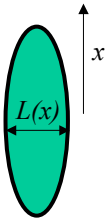
Passive mode-locking:

introduce cavity losses which can be overcome if a pulse should propagate (e.g. Kerr-lens or saturable absorber)

The principle of Kerr-lens mode-locking

A lens is a lens because the phase delay seen by a beam varies with x:

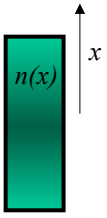
$$\phi(x) = n\, k\, L(x)$$



In both cases, a quadratic variation of the phase with x yields a lens.

What if L is constant, but n varies with x?

$$\phi(x) = n(x)\, k\, L$$



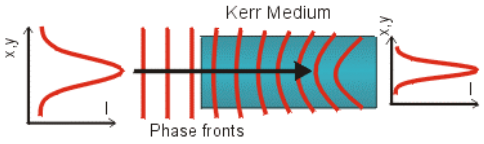
Ultra fast optical spectroscopy

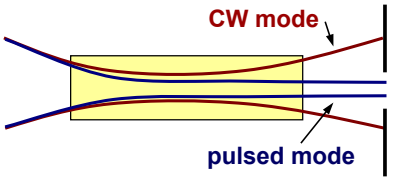
The principle of Kerr-lens mode-locking

Refractive index n for a "Kerr medium" depends on light intensity I as:

$$n(\omega, I) = n_0(\omega) + n_2(\omega)\, I$$

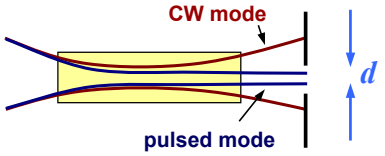
Intense pulse with spatially varying profile will experience a lens !



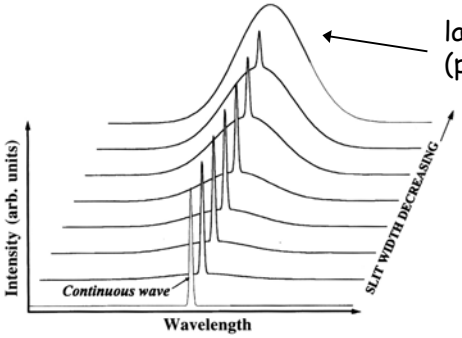


place slit in focal plane to introduce losses for CW mode

The principle of Kerr-lens mode-locking



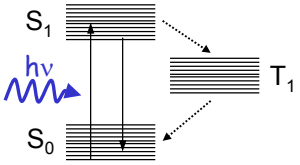
monitor the output spectrum of the laser as a function of the slit width *d*:



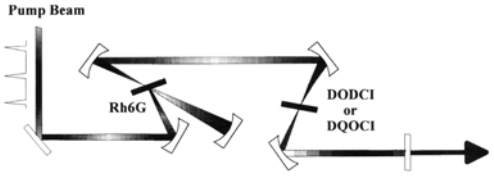
laser is mode-locked (pulsed operation)

Passive mode-locking using saturable absorbers

Use one dye as gain medium and another as saturable absorber.

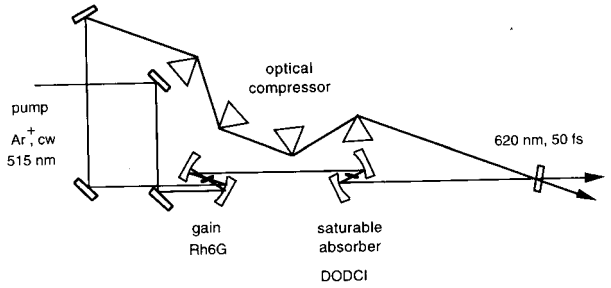


Strong excitation may "bleach" the absorption as almost all molecules transfer to the excited state
⇒ decreased losses for pulsed operation



Gain dye	Saturable absorber	Wavelength in nm
Rh6G	DODCI, DDI	575–620
Kiton Red	DQOCI	600–655
DCM	DODCI, DTDCI	620–660
Pyridine 1	DTDCI, DDI	670–740
LD 700	DTDCI, DDI, IR 140	700–800
Pyridine 2	IR 140, HITC	690–770
Styryl 9M	DDI, IR 140	780–860

Example: The Colliding-pulse mode-locked (CPM) dye laser



- Produced the first sub-100fs laser pulses !
- Ring cavity: two counter-propagating pulse trains meet in the saturable absorber
- Two prism pairs to compensate for dispersion of optical media inside cavity
- Use of dye jets results in noise

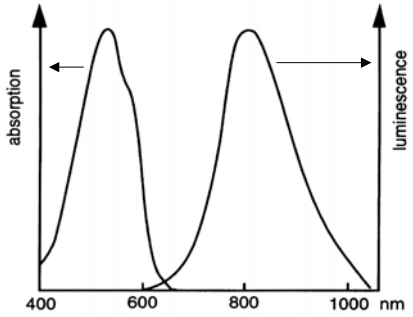
Ultra fast optical spectroscopy

Example: The mode-locked Ti:Sapphire laser (todays "work horse")

- Ti^{3+} ions can replace up to 0.1% of Al^{3+} ions in Al_2O_3 (Sapphire)
- ionic radius of Ti^{3+} 26% larger than that of Al^{3+}
- strong distortion of local environment → strong local fields which split excited state into sublevels
- ground and excited state strongly coupled to Sapphire matrix → strong electron-phonon coupling

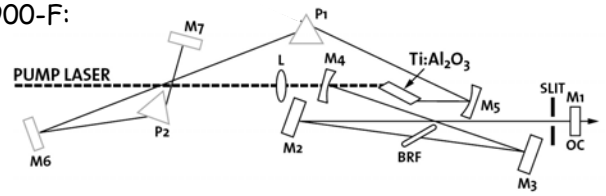
⇒ VERY broad gain medium (≥200nm)

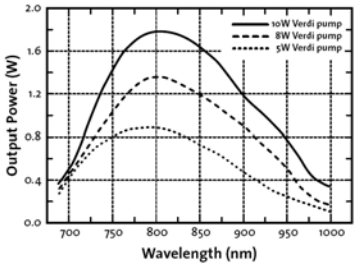
Absorption and emission spectra of Ti:Sapphire



Commercially available mode-locked Ti:Sapphire lasers

Coherent MIRA 900-F:



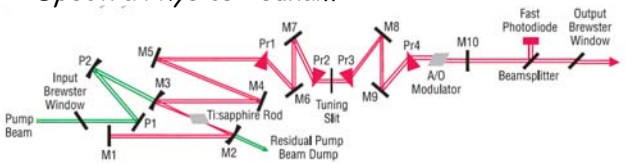


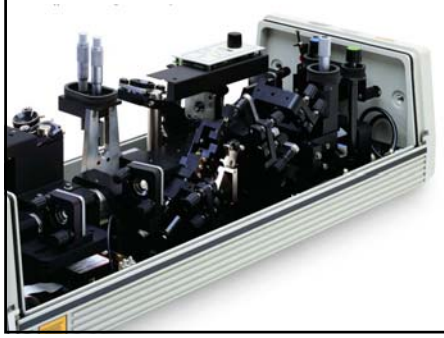
Output Power[2,3]	
(Verdi™- V5 pump)	0.65 W
(Verdi-V8)	1.0 W
(Verdi-V10)	1.3 W
(Innova® 310 8 W)	0.8 W
Sabre® 14 W	1.4 W
Tuning Range[4]	700 to 980 nm
(700 to 1000 nm typical)	
Autocorrelation[5]	<200 fs

Ultra fast optical spectroscopy

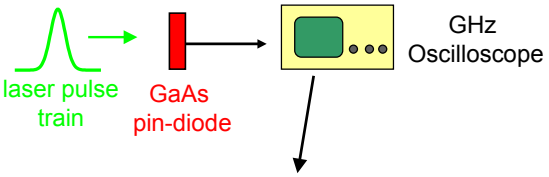
Commercially available mode-locked Ti:Sapphire lasers

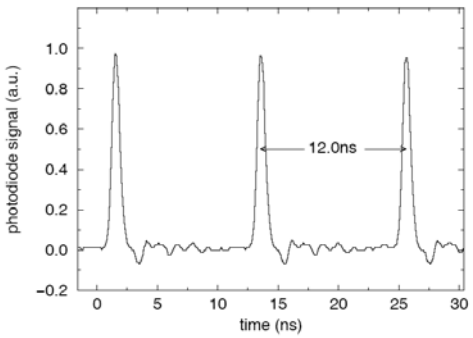
Spectra Physics Tsunami:





Measurement of the pulse duration

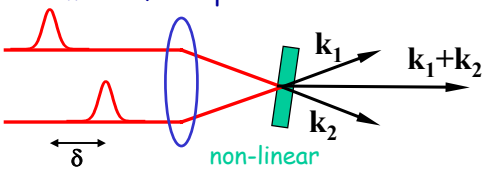




Time resolution of (at most) ≈50ps

→ not sufficient to measure 100fs pulses !

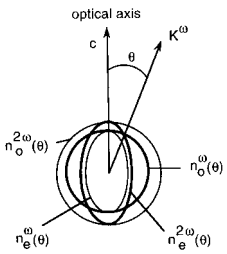
Measurement of the pulse duration: Auto-correlation



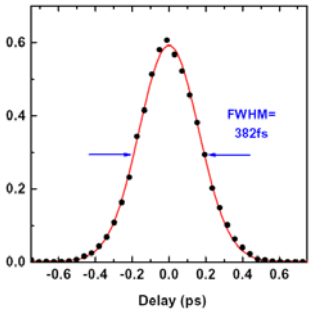
non-linear crystal (e.g. BBO)

Crystal requirements:

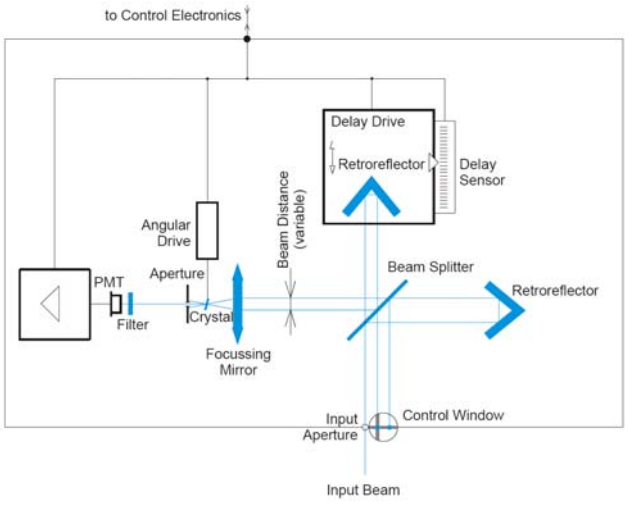
- Optical non-linearity, i.
  $P = \epsilon_0 \left(\chi E + \chi^{(2)} E^2\right)$
- Phase-matching of fundamental and 2nd harmonic (anisotropic crystal)



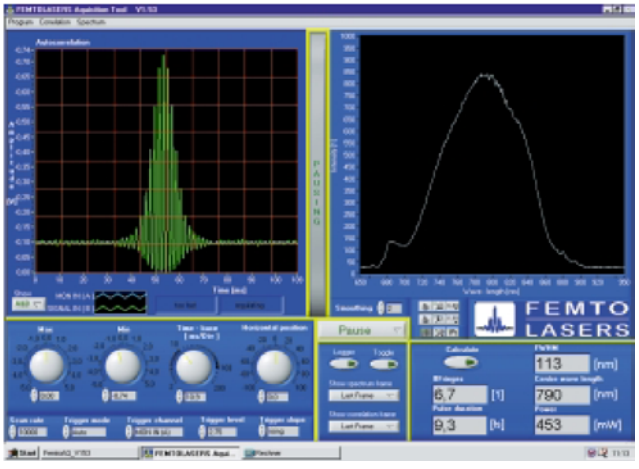
autocorrelation trace:



Measurement of the pulse duration: Auto-correlation set-up

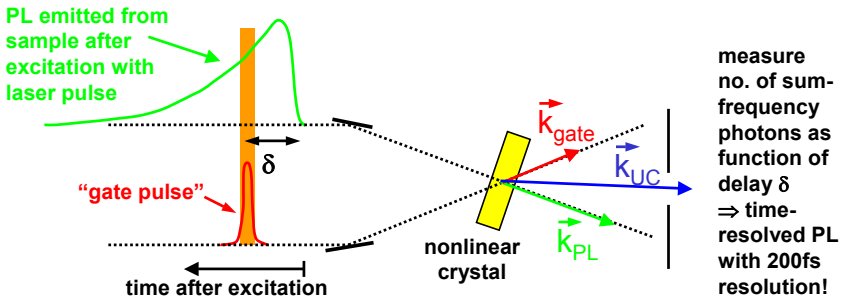


Auto-correlators are commercially widely available and typically allow measurement of pulse duration and spectrum :



Photoluminescence up-conversion (PL UC)

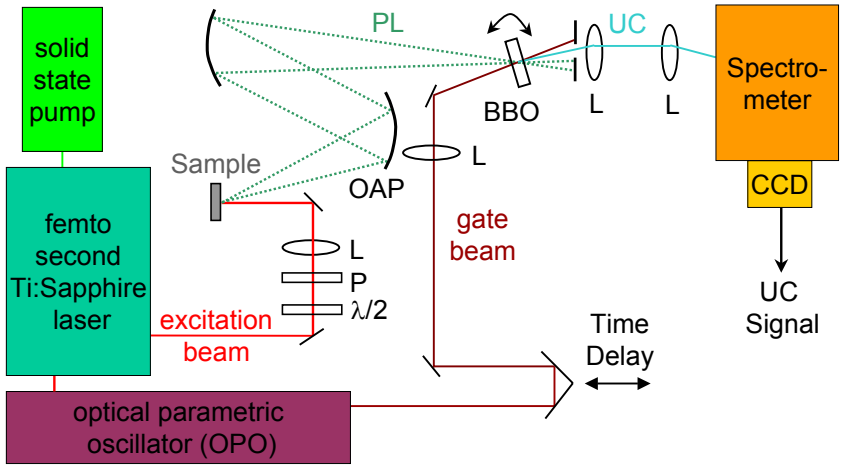
Working principle: "gating" of PL in non-linear crystal using intense gate pulse



Ultra fast optical spectroscopy

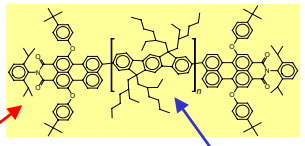
Photoluminescence up-conversion (PL UC)

Aim: Measurement of PL with time-resolution of ≈200fs



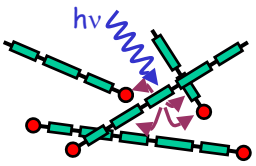
Photoluminescence up-conversion (PL UC)

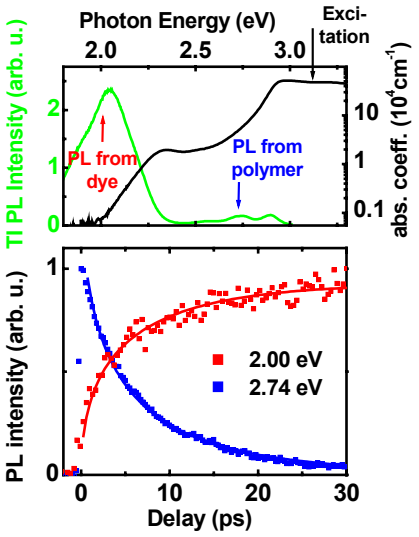
Example: Investigation into energy transfer in thin films of semiconducting polymer



Perylene Mono-imide End caps

Polyindenofluorene π-conjugated backbone (≈ 30 repeat units)

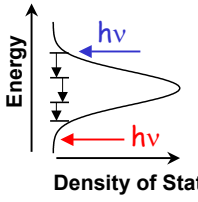




Two-colour up-conversion: allowing investigation of resonant processes

Example: Observation of resonant Rayleigh scattering from localized excitons in a semiconducting polymer (PPV)

Decoherence time (≈ 400fs) corresponds well with more recent measurements of the homogeneous linewidth (≈ 2.5 meV, Müller et al. PRL 91 267403 (2003))



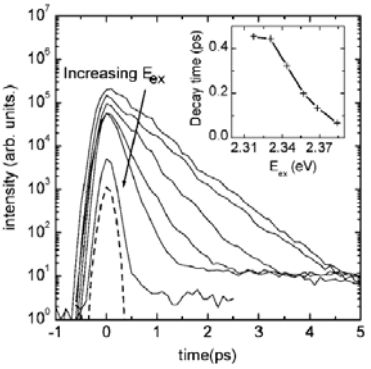
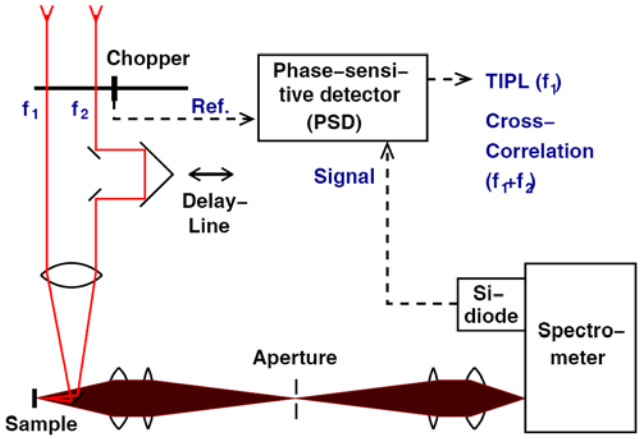


FIG. 3. Decay of the resonant emission for excitation energies 2.317, 2.330, 2.344, 2.357, 2.368, and 2.385 eV. The decay times resulting from single-exponential fits to the data are shown in the inset.

Kennedy *et al.* PRL **86** 4148 (2001)

Photoluminescence cross-correlation: set-up

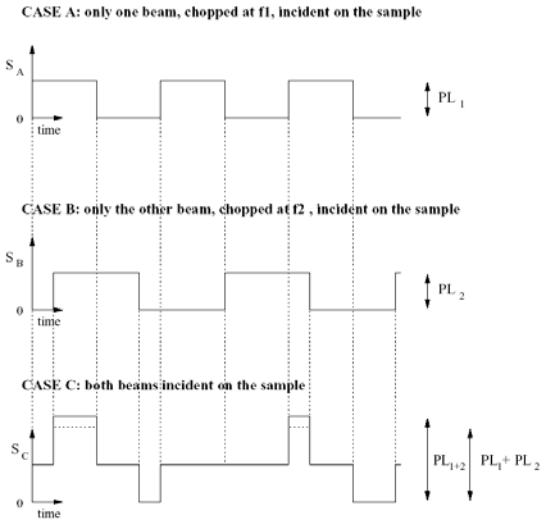


Photoluminescence cross-correlation: working principle

$$S_c = \underbrace{PL_1\, c(f_1,t) + PL_2\, c(f_2,t)}_{linear\ part\ of\ signal\ (caseA+caseB)} + \underbrace{(PL_{1+2} - PL_1 - PL_2) \times c(f_1,t)\ c(f_2,t)}_{non-linear\ part\ of\ signal}$$

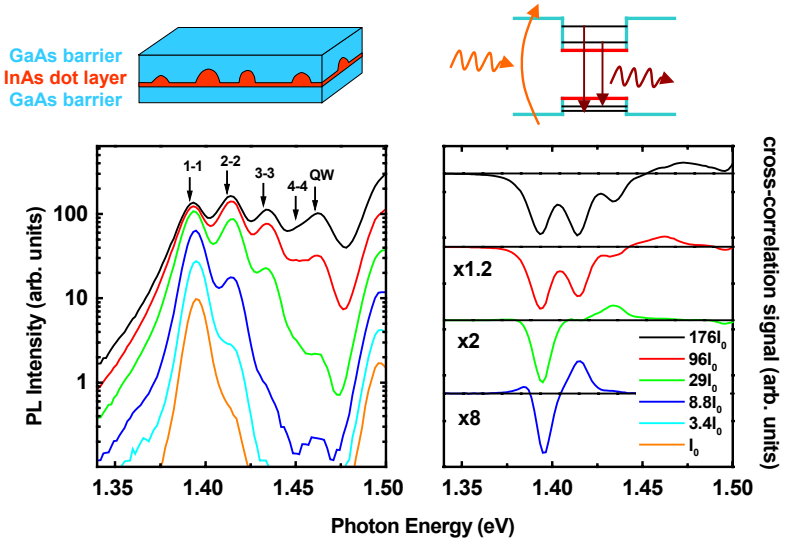
$$S_{PEC}(E,\delta) = PL_{1+2}(E,\delta) - 2\,PL_1(E,\delta)$$

⇒ PL X-correlation signal gives the influence the presence of the first pulse has on the PL generated by the second pulse



Photoluminescence cross-correlation

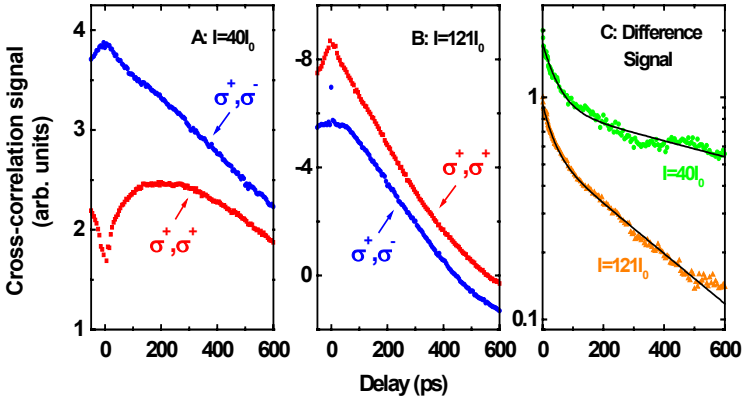
Observation of state-filling effects in self-assembled InAs quantum dots



Ultra fast optical spectroscopy

Photoluminescence cross-correlation

Observation of state-filling effects in self-assembled InAs quantum dots

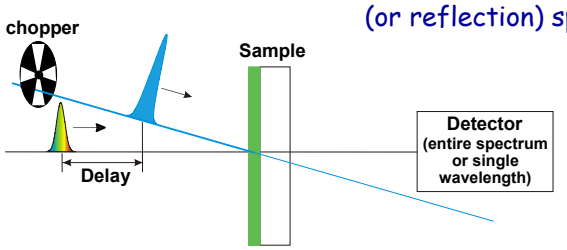


Exciting the barrier now with circularly polarized light will produce carriers with particular spin orientation

⇒ probe sensitivity of state-filling in dots to spin statistics

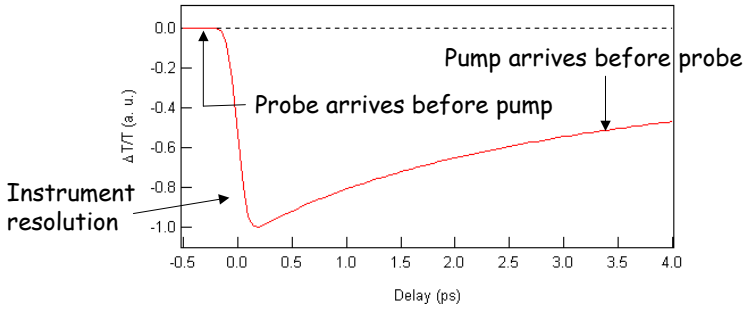
Ultra fast optical spectroscopy

Transient absorption (or reflection) spectroscopy



Change of transmission of the probe beam due to the presence of the pump beam:

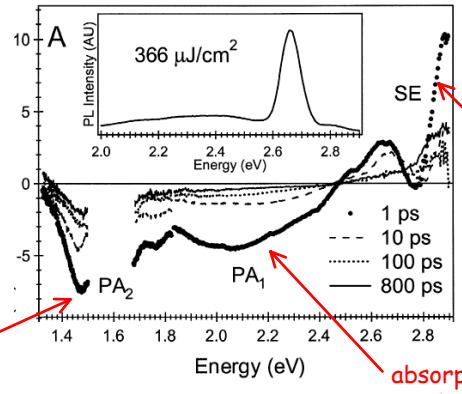
$\Delta T = T_{pump\ on} - T_{pump\ off}$



Ultra fast optical spectroscopy

Transient absorption (or reflection) spectroscopy

Example: transient probe spectra from a thin polyindenofluorene film



absorption of probe by photogenerated charges (polaron pairs of radical anion/cation intermolecular pairs)

probe stimulates emission by recombination of excitons

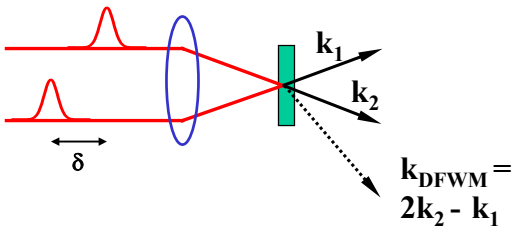
absorption of probe by excitons

Silva *et al.* Chem Phys Lett **319** 494 (2000)

Transient grating spectroscopy: Degenerate four-wave mixing

Pump photons with wavevector $\mathbf{k}_1$ generate a coherent polarization in the sample

Probe photons with $\mathbf{k}_2$ arrive after delay δ



If δ is smaller than the decoherence time of the polarization, a transient interference grating is produced, of which the probe may be deflected along the phase matched direction $\mathbf{2k_2-k_1}$.

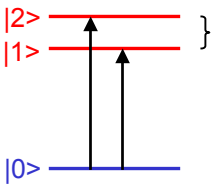
⇒ Technique of choice for investigating coherent evolution of excitations !

Transient grating (four-wave mixing) spectroscopy

In bulk GaAs light-hole (lh) and heavy-hole (hh) bands are degenerate at the Γ point.

Confinement (i.e. in a quantum well) lifts the degeneracy.

⇒ Can observe "quantum beats" (interference) between lh-e and hh-e transitions until the system is dephased !



hh-lh splitting ΔE (typ. few meV)

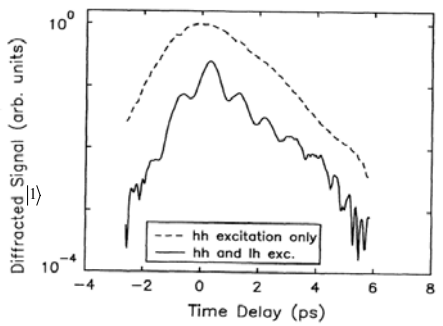
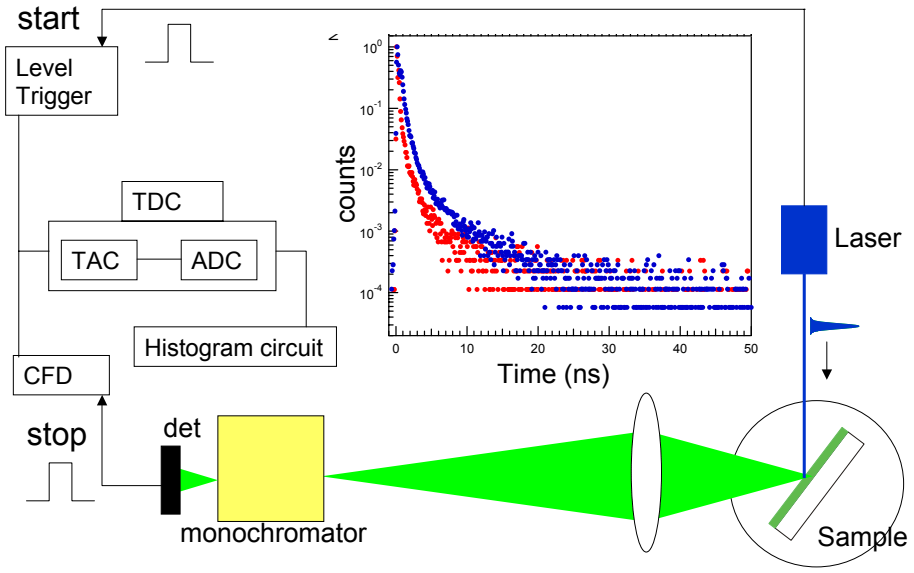


FIG. 8. Four-wave-mixing line shapes for the 170-Å quantum-well sample for excitation of the heavy-hole transition only (dashed line) and simultaneous excitation of heavy-hole and light-hole transitions (solid line). Lattice temperature ($T_L = 5$ K) and intensity (~ 160 kW cm^{-2}) are kept low.

Leo *et al.* PRB **44** 5726 (1991)

Time-correlated single photon counting (TCSPC)

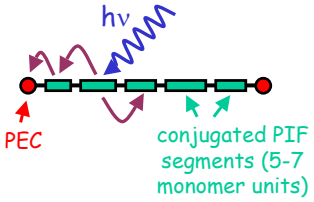


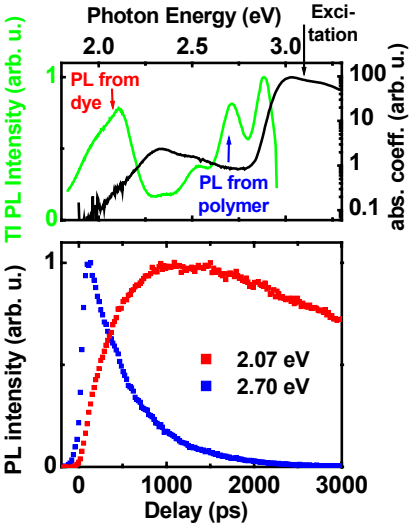
(Ultra)fast optical spectroscopy

Time-correlated single photon counting (TCSPC)

Typical time-resolution: 50ps, i.e. much worse than PLUC, but TCSPC is significantly more sensitive

⇒ Use it to observe slower processes involving low PL intensities, e.g. on-chain transfer of photoexcitations in semiconducting polymers in solution:





Time-resolving luminescence with a Streak Camera

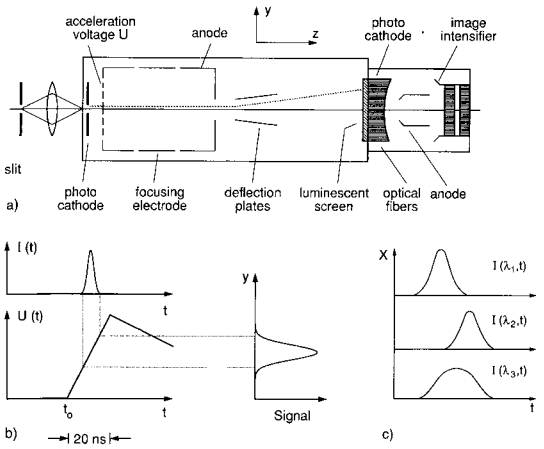


Fig. 11.39a–c. Streak camera. (**a**) Design and (**b**) schematic diagram of the relation between the time profile $I(t)$ and the spatial distribution $S(y)$ at the output plane; (**c**) spectrally resolved time profiles $I(\lambda, t)$

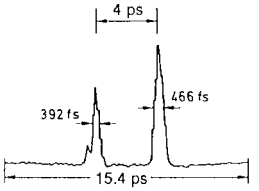


Fig. 11.40. Streak image of two subpicosecond pulses separately by 4 ps, measured with the femtosecond streak camera [11.101]