“Leading edge experimental techniques”:

Ultra fast optical spectroscopy

Laura Herz

Outline

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      • Active/passive techniques
   ii. Pulse characterization
3. Ultra fast spectroscopic techniques
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   iii. Transient absorption/reflection
   iv. Transient grating techniques
4. Not-quite-so-fast techniques
Ultra fast optical spectroscopy

**Why ultra fast?**

Relaxation processes in photoexcited matter:

- Optical phonon scattering
- Acoustic phonon scattering
- Intervalley scattering
- Carrier-carrier scattering
- Carrier recombination
- Electronic relaxation
- Nuclear relaxation
- Charge transfer

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>1 fs</th>
<th>1 ps</th>
<th>1 ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>10^{-15}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10^{-12}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10^{-9}</td>
<td></td>
<td></td>
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</tbody>
</table>

Due to these processes, relaxation times are on the order of 10 fs - 1 ps.

**Definition of “ultra fast”**: The term “ultra fast” currently implies a timescale of ≈ 10 fs - 1 ps.

**Examples of ultra 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 a short laser pulse
2. Probe the dynamics of a process with a second pulse

Delay δ
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Longitudinal modes in a laser cavity:

\[ \lambda \]

For a cavity mode to be sustained we need:

\[ 2L = q\lambda \]

⇒ Frequency spacing of longitudinal modes:

\[ \Delta \nu = \frac{\nu_{q+1} - \nu_q}{c} = \frac{\lambda_{q+1}}{c} - \frac{\lambda_q}{c} = \frac{2L}{c} \]

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
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Take a laser sustaining two longitudinal modes:

\[ E_1 = \hat{E} \cos(\omega_0 t + \varphi_0(t)) \]
\[ E_2 = \hat{E} \cos(\omega_0 + 1 \cdot t + \varphi_{0+1}(t)) \]

Output Intensity is the square of the sum:

\[ I = (E_1 + E_2)^2 \]
\[ = 4\hat{E}^2 \sin^2 \left[ \frac{\omega_0 + 1 - \omega_0}{2} t + \frac{\varphi_0 + 1 - \varphi_0}{2} \right] \cos^2 \left[ \frac{\omega_0 + 1 - \omega_0}{2} t + \frac{\varphi_0 + 1 - \varphi_0}{2} \right] \]

*term varying at optical frequency \( \sim 10^{14} \text{ Hz} \)*

*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)

\[ \Delta \nu = \frac{c}{2L} \]
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Lock together a Gaussian distribution of modes:

\[ E(t) = \sum_{n=0}^{\infty} E_n \exp(i\omega_n t) \quad \text{with} \quad \omega_n = \omega_0 + n\Delta\omega \]

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

\[ E(t) = \exp(i\omega_0 t) \sum_{n=0}^{\infty} E_n \exp(in\Delta\omega t) \]

fourier transform of \( E_n \)

⇒ 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: \[ \tau_p = \frac{2\sqrt{2}}{\pi} \Delta\omega_0 \ln 2 \Rightarrow \text{pulses are the shorter, the broader the gain medium!} \]

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⇒ to generate ultra short pulses we need to use particularly broad gain media to lock together as many modes as possible
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Examples for broad gain media:

**Organic dyes:**
broad spectra caused by strong electron-phonon coupling in π-conjugated molecules

**Ion-doped crystals:**
solid-state, allowing high gains at low noise

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**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)
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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?

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

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.
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The principle of Kerr-lens mode-locking

- CW mode
- Pulsed mode
- Monitor the output spectrum of the laser as a function of the slit width $d$.

Laser is mode-locked (pulsed operation)

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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 $\Rightarrow$ decreased losses for pulsed operation

<table>
<thead>
<tr>
<th>Gain dye</th>
<th>Saturable absorber</th>
<th>Wavelength in nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rho6G</td>
<td>DODCI, DDI</td>
<td>575-620</td>
</tr>
<tr>
<td>Ktou Red</td>
<td>DQOCI</td>
<td>600-655</td>
</tr>
<tr>
<td>DCM</td>
<td>DODCI, DTDCI</td>
<td>620-660</td>
</tr>
<tr>
<td>Pyridine 1</td>
<td>DTDCI, DODI</td>
<td>670-740</td>
</tr>
<tr>
<td>LD 700</td>
<td>DTDCI, DODI, IR 140</td>
<td>700-800</td>
</tr>
<tr>
<td>Pyridine 2</td>
<td>IR 140, HITC</td>
<td>690-770</td>
</tr>
<tr>
<td>Styril 9M</td>
<td>DODI, IR 140</td>
<td>780-860</td>
</tr>
</tbody>
</table>
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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

Example: The mode-locked Ti:Sapphire laser (today’s “work horse”)

- Ti$^{3+}$ ions can replace up to 0.1% of Al$^{3+}$ ions in Al$_2$O$_3$ (Sapphire)
- Ionic radius of Ti$^{3+}$ 26% larger than that of Al$^{3+}$
- Strong distortion of local environment $\rightarrow$ strong local fields which split excited state into sublevels
- Ground and excited state strongly coupled to Sapphire matrix $\rightarrow$ strong electron-phonon coupling
  $\Rightarrow$ VERY broad gain medium ($\geq$200nm)
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Commercially available mode-locked Ti:Sapphire lasers

Coherent MIRA 900-F:

![Diagram of Coherent MIRA 900-F](image)

Output Power:

<table>
<thead>
<tr>
<th>Type</th>
<th>Output Power (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(VersaMax: YS pump)</td>
<td>0.51 W</td>
</tr>
<tr>
<td>(VersaMax: Q-switched)</td>
<td>1.6 W</td>
</tr>
<tr>
<td>(VersaMax: Q-switch)</td>
<td>1.1 W</td>
</tr>
<tr>
<td>(VersaMax 310 W)</td>
<td>0.8 W</td>
</tr>
<tr>
<td>Sabre 14 W</td>
<td>1.4 W</td>
</tr>
</tbody>
</table>

Tuning Range: 700 to 980 nm (500 to 1000 nm typical)

Autocorrelation: <200 fs

Spectra Physics Tsunami:

![Diagram of Spectra Physics Tsunami](image)
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Measurement of the pulse duration

Laser pulse train $\rightarrow$ GaAs pin-diode $\rightarrow$ GHz Oscilloscope

Time resolution of (at most) $\approx 50$ ps $\rightarrow$ not sufficient to measure 100 fs pulses!

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Measurement of the pulse duration: Auto-correlation

Crystal requirements:
- Optical non-linearity, i.e.
  
  \[ P = r_0 (\chi E + \chi^{(2)} E^2) \]
- Phase-matching of fundamental and 2nd harmonic (anisotropic crystal)

Autocorrelation trace:

FWHM $\approx$ 35 fs
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Measurement of the pulse duration: Auto-correlation set-up

Auto-correlators are commercially widely available and typically allow measurement of pulse duration and spectrum:
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Photoluminescence up-conversion (PL UC)

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

PL emitted from sample after excitation with laser pulse

"gate pulse"

time after excitation

nonlinear crystal

measure no. of sum-frequency photons as function of delay $\delta$ ⇒ time-resolved PL with 200fs resolution!

Aim: Measurement of PL with time-resolution of $\approx 200\text{fs}$
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Photoluminescence up-conversion (PL UC)

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

- Perylene Monoimide End caps
- Polyindenofluorene π-conjugated backbone (~ 30 repeat units)

![Diagram of polymer structure]

PL from polymer

Photon Energy (eV)

- 2.0
- 2.5
- 3.0

PL intensity (arb. u.)

- 10
- 1
- 0.1

Abs. coeff. (10⁴ cm⁻¹)

PL from dye

0 10 20 30

Delay (ps)

2.00 eV

2.74 eV

PL intensity (arb. u.)

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

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

![Diagram of energy levels and density of states]

Kunst et al. PRL 86 4148 (2001)
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Photoluminescence cross-correlation: set-up

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

\[
S_\text{X}(E, \delta) = PL_{1+2}(E, \delta) - 2PL_1(E, \delta)
\]

CASE A: only one beam, chopped at \(f_1\) incident on the sample

CASE B: only the other beam, chopped at \(f_2\), incident on the sample

CASE C: both beams incident on the sample
Photoluminescence cross-correlation

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

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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
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Transient absorption (or reflection) spectroscopy

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

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

Example: transient probe spectra from a thin polyindenofluorene film

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**Transient grating spectroscopy: Degenerate four-wave mixing**

- Pump photons with wavevector \( k_1 \) generate a coherent polarization in the sample.
- Probe photons with \( k_2 \) arrive after delay \( \delta \).

If \( \delta \) 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 \( 2k_2 - k_1 \).

⇒ Technique of choice for investigating coherent evolution of excitations!

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**Transient grating (four-wave mixing) spectroscopy**

In bulk GaAs light-hole (lh) and heavy-hole (hh) bands are degenerate at the \( \Gamma \) 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!

![Diagram showing hh-lh splitting and quantum beats](image)

FIG. 3. 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 \( \sim 100 \) kW/cm² are kept low.

Leo et al. PRB 44 5726 (1991)
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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:
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Time-resolving luminescence with a Streak Camera

Fig. 11.3a-e. Streak camera. (a) Design and (b) schematic diagram of the relation between the time profile $I(t)$ and the spatial distribution $X(u)$ at the output plane; (c) spectrally resolved time profiles $I(u, t)$.