Outline

- Pulse characterization revisited
  - Autocorrelation
  - FROG

- Pump-probe measurements

- Femto-chemistry

- X-ray pulse sources
Relevant Time Scales

Physically meaningful time-scales known presently cover from $10^{-43}$ s to $10^{17}$ s.
Measurement Problem

- Student: How do you measure the length of something, anything?

-Advisor: Well, to measure is “to compare with something else and count how many of that other is within”

- Student: What if everything is else much longer/bigger?

- Advisor: You can always compare with itself…

- Student: But, then how can I count?

- Advisor: Well, you can correlate
Pulse Characterization with Autocorrelation
Pulse Measurement in the Time Domain: Autocorrelation

- Crossing beams in a nonlinear-optical crystal, varying the delay between them, and measuring the signal pulse energy vs. delay, yields the Intensity Autocorrelation, $A^{(2)}(t)$.

The signal field is $E(t) E(t-\tau)$. So the signal intensity is $I(t) I(t-\tau)$.

The Intensity Autocorrelation:

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

from R. Trebino’s Lecture Notes
Varying the delay yields varying overlap between the two replicas of the pulse. The intensity autocorrelation is only nonzero when the pulses overlap.

from R. Trebino’s Lecture Notes
Square Pulse and Its Autocorrelation

Pulse

\[ I(t) = \begin{cases} 
1; & |t| \leq \Delta \tau_{p\text{FWHM}}/2 \\
0; & |t| > \Delta \tau_{p\text{FWHM}}/2 
\end{cases} \]

Autocorrelation

\[ A^{(2)}(\tau) = \begin{cases} 
1 - \frac{\tau}{\Delta \tau_{A\text{FWHM}}}; & |\tau| \leq \Delta \tau_{A\text{FWHM}} \\
0; & |\tau| > \Delta \tau_{A\text{FWHM}} 
\end{cases} \]

\[ \Delta \tau_{p\text{FWHM}} = \Delta \tau_{A\text{FWHM}} \]

from R. Trebino’s Lecture Notes
Gaussian Pulse and Its Autocorrelation

\[
I(t) = \exp\left[ -\left( \frac{2\sqrt{\ln2}t}{\Delta \tau_{FWHM}^p} \right)^2 \right]
\]

\[
A^{(2)}(\tau) = \exp\left[ -\left( \frac{2\sqrt{\ln2}\tau}{\Delta \tau_{FWHM}^A} \right)^2 \right]
\]

\[
1.41 \Delta \tau_{FWHM}^p = \Delta \tau_{FWHM}^A
\]

from R. Trebino’s Lecture Notes
Sech2 Pulse and Its Autocorrelation

Pulse

\[ I(t) = \text{sech}^2 \left( \frac{1.7627 t}{\Delta t_p^{\text{FWHM}}} \right) \]

Autocorrelation

\[ A^{(2)}(\tau) = \frac{3}{\sinh^2 \left( \frac{2.7196 \tau}{\Delta \tau_A^{\text{FWHM}}} \right)} \left[ \frac{2.7196 \tau}{\Delta \tau_A^{\text{FWHM}}} \coth \left( \frac{2.7196 \tau}{\Delta \tau_A^{\text{FWHM}}} \right) - 1 \right] \]

from R. Trebino’s Lecture Notes
Problem: Autocorrelations have ambiguities

These intensities have the same, nearly Gaussian, autocorrelations.

Retrieving the intensity from the autocorrelation is equivalent to the 1D Phase-Retrieval Problem, a well-known unsolvable problem.

from Selçuk Aktürk
Advanced Pulse Characterization Techniques
Acoustic Waves: Musical Score

It’s a plot of frequency vs. time, with info on top about intensity.

The musical score lives in the “time-frequency domain.”

from Selçuk Aktürk
If \( E(t) \) is the waveform of interest, its spectrogram is:

\[
\Sigma_E(\omega, \tau) \equiv \left| \int_{-\infty}^{\infty} E(t) g(t - \tau) \exp(-i\omega t) \, dt \right|^2
\]

where \( g(t-\tau) \) is a variable-delay gate function and \( t \) is the delay.

Without \( g(t-\tau) \), \( \Sigma_E(\omega, \tau) \) would simply be the spectrum.

The spectrogram is a function of \( \omega \) and \( \tau \).

It is the set of spectra of all temporal slices of \( E(t) \).
We must compute the spectrum of the product: \( E(t) g(t-\tau) \)

The spectrogram tells the color and intensity of \( E(t) \) at the time, \( \tau \).

Example: Linearly chirped Gaussian pulse
Like a musical score, the spectrogram visually displays the frequency vs. time (and the intensity, too).

from Selçuk Aktürk
Properties of the Spectrogram

Algorithms exist to retrieve $E(t)$ from its spectrogram.

The spectrogram essentially uniquely determines the waveform intensity, $I(t)$, and phase, $\phi(t)$.

There are a few ambiguities, but they’re “trivial.”

The gate need not be—and should not be—much shorter than $E(t)$.

Suppose we use a delta-function gate pulse:

$$\left| \int_{-\infty}^{\infty} E(t) \delta(t - \tau) \exp(-i\omega t) \, dt \right|^2 = \left| E(\tau) \exp(-i\omega \tau) \right|^2$$

$$= \left| E(\tau) \right|^2 = \text{The Intensity.}$$

No phase information!

The spectrogram resolves the dilemma! It prefers not to have the shorter event! It temporally resolves the slow components and spectrally resolves the fast components.

from Selçuk Aktürk
Frequency-Resolved Optical Gating (FROG)

FROG involves gating the pulse with a variably delayed replica of itself and then spectrally resolving the gated pulse vs. delay.

Use any ultrafast nonlinearity: Second-harmonic generation, etc.

\[ I_{FROG}(\omega, \tau) = \left| \int_{-\infty}^{\infty} E_{\text{sig}}(t, \tau) \exp(-i\omega t) \, dt \right|^2 \]

\[ E_{\text{sig}}(t, \tau) = E(t) \, |E(t-\tau)|^2 \]
The gating is more complex for complex pulses, but it still works. And it also works for other nonlinear-optical processes.

\[ |E(t - \tau)|^2 \] gates out a piece of \( E(t) \), (centered at about \( 2\tau/3 \) for Gaussian pulses).

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**Frequency-Resolved Optical Gating (FROG)**

From Selçuk Aktürk
Like a musical score, the FROG trace visually reveals the pulse frequency vs. time—for simple and complex pulses.
Phase Retrieval from FROG

- It is not enough to record the measurement, the pulse profile has to be computed.

- This is not trivial and an iterative computation is required.

- There are other techniques, such as SPIDER, where retrieval is easy, but the setup is complicated.

- Most people still prefer autocorrelation for its simplicity… Sufficient if pulses are not too complicated.
Spectral Phase Interferometry for Direct Electric—Field Reconstruction (SPIDER )

Figure 10.13: SPIDER setup; SF10: 65 mm glass block (GDD/z ≈ 160 fs²/mm), BS: metallic beam splitters (≈ 200 μm, Cr–Ni coating 100 nm), τ: adjustable delay between the unchirped replica, τ_{SHG}: delay between unchirped pulses and strongly chirp pulse, RO: reflective objective (Ealing–Coherent, x35, NA=0.5, f=5.4 mm), TO: refractive objective, L: lens, spectrometer: Lot-Oriel MS260i, grating: 400 l/mm, Blaze–angle 350 nm, CCD: Andor DU420 CCI 010, 1024 x 255 pixels, 26 μm/pixel [4].
SPIDER for 5 fs pulses
Ultrafast Measurements:
Ultrafast Spectroscopy
(most slides adopted from R. Trebino)
Motivation

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:

\[ \frac{1}{\tau_{ex}} = \frac{1}{\tau_{fl}} + \frac{1}{\tau_{nr}} \]

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.
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.
The excite pulse(s) excite(s) molecules into excited states, which changes the medium’s absorption coefficient and refractive index. The excited states only live for a finite time (this is the quantity we’d like to find!), so the absorption and refractive index recover.
Simplest Technique: Pump-probe Measurements

Excite the sample with one pulse; probe it with another a variable delay later; and measure the change in the transmitted probe pulse energy or average power vs. delay.

The excite pulse changes the sample absorption seen by the probe pulse.

The excite and probe pulses can be different colors. This technique is also called the “Pump-Probe” Technique.
More complex decays can be seen if intermediate states are populated or if the motion is complex. Imagine probing an intermediate transition, whose states temporarily fill with molecules on their way back down to the ground state:

![Diagram showing energy levels and transitions](image)

- **Excite transition**: Absorption of probe
- **Probe transition**: Change in probe-beam transmitted intensity or power

- **Excited molecules in state 1**: Absorption of probe
- **Excited molecules in state 2**: Stimulated emission of probe

Graph showing change in probe-beam transmitted intensity or power over delay, \( \tau \):
Pump-probe Measurements of Glass

- S. Smolorz PhD thesis:

Figure 5.3: SRTBC signal of pure fused silica, obtained at a detuning of \(~0.7\) FWHM. The solid line is the experimental signal, the broken line is the calculation.
This involves **chopping** the excite pulse at a given frequency and detecting at that frequency with a lock-in detector:

The excite pulse **periodically** changes the sample absorption seen by the probe pulse.

Lock-in detection automatically subtracts off the transmitted power in the absence of the excite pulse. With high-rep-rate lasers, it increases sensitivity by **several orders of magnitude**!
DNA bases undergo photo-oxidative damage, which can yield mutations. Understanding the photo-physics of these important molecules may help to understand this process.

**Fig. 1.** Transient absorption at 600 nm of protonated guanosine in acidic (pH 2) and basic (pH 11) aqueous solution

Since ultrashort pulses have broad bandwidths, they can excite two or more nearby states simultaneously. Probing the 1-2 superposition of states can yield quantum beats in the excite-probe data.
Here, two nearby vibrational states in molecular iodine interfere. These beats also indicate the motion of the molecular wave packet on its potential surface. A small fraction of the I$_2$ molecules dissociate every period. 

Vibrational relaxation and predissociation in the B state of iodine, in solid Kr. Pump at 545 nm, probe at 395 nm.

Time-resolved fluorescence

Exciting a sample with an ultrashort pulse and then observing the fluorescence vs. time also yields sample dynamics. This can be done by directly observing the fluorescence or, if it’s too fast, by time-gating it with a probe pulse in a SFG crystal:
Other ultrafast spectroscopic techniques

Photon Echo

Transient Coherent Raman Spectroscopy

Transient Coherent Anti-Stokes Raman Spectroscopy

Transient Surface SHG Spectroscopy

Transient Photo-electron Spectroscopy

Almost any physical effect that can be induced by ultrashort light pulses!