Generally you have some “stuff” and you want to know something about the dynamics of the stuff.

Kick the stuff with an “excitation” or “pump” pulse which triggers some dynamical process.

Wait a little while and then fire a “probe” or “test” pulse at the stuff.

This causes the stuff to emit light (could just be the probe pulse itself) which you then detect.
Nonlinear spectroscopy

Most ultrafast spectroscopy techniques are a form of “nonlinear spectroscopy”

**Linear**: absorption, reflection, fluorescence/luminescence

**Nonlinear**: two or more laser beams interact with each other in the sample

Interaction only occurs if the response of the sample to light is nonlinear
(otherwise superposition principle holds)

Why use nonlinear spectroscopic techniques?

Because they produce more information, for example:

- Homogeneous linewidth in an inhomogeneously broadened sample
- Dynamics such as relaxation or diffusion
- Coupling or lack of coupling between resonances
- Access to multiply excited states or forbidden transitions

They generally require relatively high intensities in at least on beam, thus only possible using lasers

Generally can be implemented in either time or frequency domains.
Time versus frequency

Time

Vary delay between pulses in two beams

Easy: short delays (< 1 ns)

Hard: large delays (> 5 ns)

Frequency

Vary frequency difference between two CW beams

Easy: small detunings (< 1 GHz)

Hard: Large detunings (> 3 GHz)

Conclusion

Better for fast processes  Better for slow processes

Furthermore: consider what happens when there are two timescales:

Exponential Decays with fast timescale

Lorentzians with widths inversely proportional to slow timescale

Tends to get lost in the noise

More sensitive to fastest process

More sensitive to slowest process
Incident pulses

What is the optimum duration for the incident pulses?

“Hey …this is ultrafast, isn’t the shortest possible pulse always the best?”

….is it?.....

No. Generally not.

Generally the best is to use the longest pulse you can get away with: it needs to be short enough to resolve the fast dynamics, but no shorter.

Why?

1) It will “drive” the system better.
   Spectral domain: better overlap between pulse spectrum and absorption spectrum
   Time domain: coherently build up excitation up to dephasing time (1/linewidth)

2) Give some ability to spectrally select the resonance of interest
   Most of the time there are other states/transitions at different energies, exciting them can lead to confusion.
Detection can generally be categorized as (in increasing order of difficulty):

1) Time & spectrally integrated
   Detect energy of emitted signal pulses
   Average over many pulses

2) Spectrally resolved
   Typically just a grating spectrometer

3) Temporally resolved
   Usually done with cross correlation, cross-FROG

4) Full characterization of electric field
   Spectral interferometry with phase locked reference pulse

Spectrally or Temporally resolved detection provides more information, and are typically related (FT)

Question: Do they provide useful additional information?

Answer: It depends....
Incoherent versus coherent spectroscopy

Incoherent: only sensitive to “population” relaxation \(\rightarrow\) rate equations sufficient

Examples:
- Time resolved fluorescence/luminescence
- Transient absorption
- Spectrally resolved transient absorption
- Transient grating

Coherent: also sensitive to phase relaxation \(\rightarrow\) Optical Bloch Equations needed

Example:
- Transient Four-wave Mixing (a.k.a. Photon Echoes)
- Two-dimensional Fourier Transform spectroscopy
Time resolved fluorescence/luminescence

Only technique that

- Uses a single pulse
- Is linear

Excite high lying state/band with short pulse

Time resolve spontaneously emitted fluorescence from lower state

Energy difference of absorbed and emitted photon needed to distinguish scattered pump photons from spontaneously emitted photons

Rise time of fluorescence gives $\gamma_{21}$

Decay gives $\gamma_{10}$

Challenge: detection with sufficient time resolution

1) Time-correlated photon counting
2) Streak camera
3) Up-conversion/cross-correlation
Time-correlated single photon counting I

1) Excite sample with short pulses
2) Collect less than 1 photon of fluorescence per pulse
3) Record time of arrival (relative to excitation pulse) of fluorescence photons
4) Repeat and build up histogram of arrival times (#photons per time bin)

Challenges:
- Temporal dispersion in single photon detector
  - PMT
  - Microchannel plate
- Temporal dispersion in spectrometer
- Amplitude fluctuations
  - Use constant fraction discriminator
Measurement is convolution of actual decay function with system response function

\[ H(\tau) \propto \int S(\tau - t)G(t)dt \]

- \( H(\tau) \) – measured histogram
- \( S(\tau) \) – system response function
- \( G(\tau) \) – Fluorescence decay function

Generally
1) assume functional form for \( G(\tau) \) (multi-exponential)
2) fit \( H(\tau) \)
3) using a measured \( S(\tau) \) (use scatterer – instantaneous)

Best achieved time resolution with MCP \( \sim 30 \) ps
Streak camera

Convert light to electrons
Use electric field ramp to streak electrons across phosphor screen
  Synchronize ramp to excitation pulse
Converts time to space
Similar technology to oscilloscope
  Often use 2D screen, wavelength in other axis
Best time resolution: 200 fs
Typical resolution: few ps

Typical results
  Note rise time for horizontal polarized, time for molecules to reorient
Cross-correlation between fluorescence and a reference pulse

Overlap in second harmonic crystal, detect sum frequency light as function of reference pulse delay

Excellent time resolution limited only by:
- Pulse duration
- Geometric considerations in overlap

Limitation:
- Limited “acceptance angle” of phase matching

Transient Absorption

Standard explanation:

Absorption of a two level system is proportional to $n_0 - n_1$

If the pump pulse excites population into upper state, $n_0$ decreases, $n_1$ increases, so absorption decreases.

Signal as a function of delay gives relaxation rate of upper state back to lower state

Signal is

$\Delta T = (\text{transmission of probe with pump}) - (\text{transmission of probe without pump})$

This is implemented using an optical chopper and lockin detection

Typically actual measurement is

$$\frac{\Delta T}{T} = e^{-\Delta \alpha} - 1 \approx \frac{S_{\text{lockin}}}{\langle I_{\text{DET}} \rangle}$$

Directly related to change in absorption coefficient, easy to measure
Transient Absorption

Generally keep probe weaker than pump
  (not needed in “$\chi^{(3)}$” regime)

Signal should be
  Proportional to pump intensity
  Proportional to probe intensity
Spectrally resolved Transient Absorption

Similar to transient absorption, but take spectrum of transmitted probe at each delay

Again take difference between spectrum with pump and without pump

Particularly effective for tracking excitation in bands

For resonances:

Sensitive to, and can differentiate between, more mechanisms than just “saturation” (also known as bleaching)

- Bleaching: change in oscillator strength
- Broadening: change with linewidth
- Spectral shift: change in center frequency
Spectrally resolved transient absorption lineshapes

Each mechanism gives different lineshape

Note: Area is zero for broadening or spectral shift → no signal for spectrally integrated

\[
P(\omega) \sim \frac{1}{2\pi} \frac{f\Gamma}{(\omega - \omega_0)^2 + \Gamma^2/4}
\]
Transient Absorption: Excited state absorption

Additional signal due to excited state absorption

Induced absorption because transitions to higher lying states becomes allowed
Transient grating

Interfere two beams: form grating in excited state population.
Decays due to:

- Relaxation from upper to lower state
- And, due to diffusion with decay constant

\[ \Gamma_D = \frac{4\pi^2 D}{\Lambda^2} \]

Where \( D \) is diffusion rate, \( \Lambda \) is inverse grating spacing
Raman Scattering

The frequency of light can shift on scattering from a medium
Leaves an “excitation” behind in the medium to conserve energy
  Molecular vibration
  Phonon
  Magnon
  etc…

First observed in 1928 by C.V. Raman (on February 28th, to be exact)
Used sunlight (no lasers in 1928)
Tends to be a very weak effect
  So lasers helped a lot….  

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Incident “pump” photon  
Raman photon  
Energy of “excitation”
Typical Spontaneous Raman Scattering Experiment

Relatively high power laser

Really, really good monochrometer
  Raman shifts are typically relatively small
  Raman effect is weak
  Difficult to separate Raman signal from incident laser light
  Typically requires photon counting level detection

Raman spectra give
  Energy of “excitation”
  Width (= lifetime) of excitation
**Raman vs. Fluorescence**

Fluorescence can also produce light of a different color
leaves atom in an excited state
…or…heats material (relaxation in upper state)

How do you distinguish between Raman and Fluorescence?

1) Raman does not require a “real” upper state

2) Raman is a coherent and “instantaneous” process

3) Raman intensity scales as $\omega^4$

4) Raman obeys “strict” selection rules in polarization and momentum

5) Raman transitions are not optically allowed

“Resonant” Raman blurs these distinctions
Stimulated Raman

In “Stimulated” Raman, the laser field(s) drives both transitions

This creates coherence among the excitations

The coherence is then probed with another laser field (could actually be same laser)

Observed as a higher order scattering process “Anti-Stokes Raman Scattering”

Or by change in properties of other laser field, usually phase

Ultrafast pulses:

can have enough bandwidth that both photons come from a single pulse

This means that the pulse duration is shorter than one oscillation of the “excitation”

Impulsive regime: pulse is more than a factor of 2 shorter

In molecules this means that multiple vibrational levels are excited and a “wavepacket” is created
Molecular vibrations: driving pulse

Short pulse starts the molecule vibrating
  Oscillations in the THz frequency range

Semi-classically:
  Impulsive kick
  Occurs because pulse mixes in excited state with
  shifted potential minimum

Quantum Mechanically:
  Raman Transition between vibrational quantum states
Detection with a probe pulse

Classical picture:
- Polarizability of bond depends on intranuclear separation
- Polarizability is responsible for index of refraction → vibration corresponds to oscillating bond length which results in oscillating index of refraction
- Oscillating index of refraction phase modulates pulse
- Pulse is shorter than oscillation time → pulse sees phase ramp, which is frequency shift
- Narrow filter converts oscillating frequency into amplitude
- Example at right shows opposite sides of probe spectrum

Quantum picture:
- Raman transitions
- Alternates between Stokes and anti-Stokes depending on phase of Raman coherence

Optical Phonons

Similar to molecular vibrations
Effectively molecules on lattice
Optical phonons basically don’t propagate
Short pulse excites phonon
Effectively standing wave
Called “Coherent Phonons”
Often use “spectrally resolved” detection
Example of coherent phonons

Phonons in LaAlO$_3$

Transmission signal
due to "boundary" effects
i.e., change in reflectivity
Shows temperature dependence of
Phonon frequency (earlier slide)
Phonon decay rate
Both compare well with Raman scattering

Magneto-Optical Faraday Effect

Observed by Faraday in 1845

The polarization of light propagating parallel to a magnetic field in a material rotates

- magnitude of rotation proportional to field
- rotation direction depends of field direction, not propagation direction

Simple classical description for transparent materials:

- Decompose linearly polarized light into left and right handed circular components
- Circular component makes electron execute circular motion
- Magnetic field either causes the orbit radius to increase or decrease depending on direction relative to field
  - Increase in radius means stronger interaction $\rightarrow$ larger index of refraction
  - Decrease in radius means weaker interaction $\rightarrow$ smaller index of refraction

Difference in refraction corresponds to a relative phase shift, resulting in rotation of linear polarization
Magneto-optical Kerr Effect

Observed by Rev. John Kerr in 1877

Reflected linearly polarized light off of polished electromagnet pole

- Observed that the polarization rotated
- Amount of rotation proportional to field
- Rotation direction switched with a switch in field direction

Basically, the magneto-optic Kerr effect is the reflected version of the magneto-optic Faraday effect

In both Faraday and Kerr effects there is both a

- Rotation of the polarization direction
  and
- Change in ellipticity

These have opposite origins in the two cases…
Transient Faraday/Kerr Effect

In ultrafast, the photo-Faraday or Kerr effect is of interest

The broken symmetry between right and left handed components is induced by light

   Due to a pump, which is generally circularly polarized

   Simplest case: resonances that differ in angular momentum, circularly polarized pump saturates one of them

Furthermore, if that is done with a short pulse, we can watch relaxation

   Example: spin flips of electrons

A magnetic field is generally not required, although one may be used
Resonant Faraday and Kerr effect

Consider the absorption and index of refraction for a simple resonance

For no magnetic field both helicities see same resonance

Static magnetic field
Zeeman effect will shift one up in frequency the other down
This creates a difference in index (and absorption) for light of a single frequency
Taking the difference between right and left gives the Faraday and Kerr effects
Faraday rotation: Difference between index
Faraday ellipticity: Difference between absorption
Kerr ellipticity: difference between index
Kerr rotation: difference between absorption
Circularly polarized pump beam creates excitation of one handedness

Saturates that resonance

or, creates effective magnetic field (aligned spins)

or, there is spin-dependent scattering

Measure signal as a function of delay between pump pulse and probe pulse

Data at right shows signal when applied magnetic field is perpendicular to propagation direction

electrons precess around field

precession frequency yields $g$-factor

$$\Omega_L = \frac{g^e_{\text{eff}} \mu_B H_x}{\hbar}$$
There is clearly a close connection between Faraday/Kerr rotation or ellipticity and transient absorption.

Faraday/Kerr rotation is sensitive to changes in index of refraction:

- Other polarization acts as “local oscillator”

Advantages over transient absorption:

- Far off resonance, index changes are larger than absorption changes
- Utilizes “balanced” detection so amplitude fluctuations on input laser are cancelled
- Quite small rotations can be measured
Faraday rotation/ellipticity as a Raman process

It is possible to view Faraday and Kerr experiments on spin systems as Raman processes.

Lower two levels are spin up versus spin down.

Pump photon imparts angular momentum and energy necessary to make transition from spin down to spin up.
Cool example of Faraday rotation in “spintronics”

Drag spin polarized electrons using a transverse electric field

Kikkawa and Awschalom, Nature 397, 139 (1999)