Ultrafast Laser Spectroscopy

How do we do ultrafast laser spectroscopy?
Generic ultrafast spectroscopy experiment
The excite-probe experiment
Lock-in detection
Transient-grating spectroscopy
Ultrafast polarization spectroscopy
Spectrally resolved excite-probe spectroscopy
Theory of ultrafast measurements: the Liouville equation
Iterative solution – example: photon echo
Ultrafast laser 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.
What’s going on in spectroscopy measurements?

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 lifetime is often the quantity we’d like to find!), so the absorption and refractive index return to their initial (before excitation) values eventually.
The simplest ultrafast spectroscopy method is the **Excite-Probe technique**.

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 of the sample, temporarily.

The excite and probe pulses can be different colors. This technique is also called the **Pump-Probe** technique.
Modeling excite-probe measurements

Let the unexcited medium have an absorption coefficient, $\alpha_0$. Immediately after excitation, the absorption decreases by $\Delta\alpha_0$. Excited states usually decay exponentially:

$$\Delta\alpha(\tau) = \Delta\alpha_0 \exp(-\tau / \tau_{ex}) \quad \text{for } \tau > 0$$

where $\tau$ is the delay after excitation, and $\tau_{ex}$ is the excited-state lifetime.

So the transmitted probe-beam intensity—and hence pulse energy and average power—will depend on the delay, $\tau$, and the lifetime, $\tau_{ex}$:

$$I_{\text{transmitted}} = I_{\text{incident}} e^{-\left(\alpha_0 L - \Delta\alpha_0 \cdot e^{-\tau / \tau_{ex}} L\right)}$$

where $L = \text{sample length}$

$$= I_{\text{incident}} e^{-\alpha_0 L} e^{\Delta\alpha_0 \cdot e^{-\tau / \tau_{ex}} L}$$

$$\approx I_{\text{incident}} e^{-\alpha_0 L} \left(1 + \Delta\alpha_0 \cdot e^{-\tau / \tau_{ex}} L\right) \quad \text{assuming } \Delta\alpha_0 L \ll 1$$

$$\approx I_{\text{transmitted}} (\tau < 0) \left(1 + \Delta\alpha_0 \cdot e^{-\tau / \tau_{ex}} L\right)$$
Modeling excite-probe measurements (cont’d)

\[ I_{\text{transmitted}}(\tau) \approx I_{\text{transmitted}}(\tau < 0) \left(1 + \Delta\alpha_0 \cdot e^{-\tau/\tau_{ex}} L\right) \]

The relative change in transmitted intensity vs. delay, \( \tau \), is:

\[ \frac{\Delta T(\tau)}{T_0} = \frac{I_{\text{transmitted}}(\tau) - I_{\text{transmitted}}(\tau < 0)}{I_{\text{transmitted}}(\tau < 0)} \]

\[ \Rightarrow \frac{\Delta T(\tau)}{T_0} \approx \Delta\alpha_0 \cdot e^{-\tau/\tau_{ex}} L \]
Modeling excite-probe measurements (cont’d)

More complex decays occur 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:

Excited molecules in state 2: stimulated emission of probe

Excited molecules in state 1: absorption of probe
Lock-in Detection greatly increases the sensitivity in excite-probe experiments.

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.

The lock-in detects only one frequency component of the detector voltage—chosen to be that of the chopper.

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!
Rhodopsin is the main molecule involved in vision. After absorbing a photon, rhodopsin undergoes a many-step process, whose first three steps occur on fs or ps time scales and are poorly understood.

Excitation populates a new state, which absorbs at 460nm and emits at 860nm. It is thought that this state involves motion of the carbon atoms (12, 13, 14). An artificial version of rhodopsin, with those atoms held in place, reveals this change on a much slower time scale, confirming this theory!
Excite-probe measurements can reveal quantum beats

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.
Excite-probe measurements can reveal quantum beats: Experiment

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.

Time-frequency-domain absorption spectroscopy of Buckminster-fullerene

Electron transfer from a polymer to a buckyball is very fast. It has applications to photo-voltaics, nonlinear optics, and artificial photosynthesis.

The coherence spike in ultrafast spectroscopy

When the delay is zero, other nonlinear-optical processes occur, involving coherent 4WM between the beams and generating additional signal not described by the simple $\Delta \alpha$ model. As in autocorrelation, it’s called the coherence spike or coherent artifact. Sometimes you see it; sometimes you don’t.

This spike could be a very very fast event that couldn’t be resolved. Or it could be a coherence spike.

Alternate picture: the pulses induce a grating in the absorption and/or refractive index, which diffracts light from each beam into the other.
Taking advantage of the induced grating: the **Transient-Grating Technique**.

Two simultaneous excitation pulses induce a weak diffraction grating, followed, a variable delay later, by a probe pulse. Measure the diffracted pulse energy vs. delay:

This method is **background-free**, but the diffracted pulse energy goes as the square of the diffracted field and hence is weaker than that in excite-probe measurements.
A transient-grating measurement may still have a coherence spike!

When all the pulses overlap in time, who’s to say which are the excitation pulses and which is the probe pulse?

A transient-grating experiment with a coherence spike:

- Excite pulse #1 (acting as the probe)
- Excite pulse #2
- Probe pulse (acting as an excite pulse)

Intensity fringes in sample due to an excitation pulse and the probe acting as an excitation pulse

Diffracted beam energy

0  Delay, \(\tau\)
What the transient-grating technique measures

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

\[
\eta(\tau) \approx \left( \frac{\Delta \alpha(\tau) L}{4} \right)^2 + \left( \frac{\Delta n(\tau) k L}{2} \right)^2
\]

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 $\exp(-2\tau/\tau_{ex})$:

Time-resolved fluorescence is also useful.

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.
Time-resolved fluorescence decay

When different tissues look alike (i.e., have similar absorption spectra), looking at the time-resolved fluorescence can help distinguish them.

Here, a malignant tumor can be distinguished from normal tissue due to its longer decay time.

Exciting a molecule and watching its fluorescence reveals much about its potential surfaces. Ideally, one would measure the time-resolved spectrum, equivalent to its intensity and phase vs. time (or frequency).

Here, excitation occurs to a predissociative state, but other situations are just as interesting. Analogous studies can be performed in absorption.
Ultrafast Polarization Spectroscopy

A 45°-polarized excite pulse induces birefringence in an ordinarily isotropic sample via the Kerr effect. A variably delayed probe pulse between crossed polarizers watches the birefringence decay, revealing the sample orientational relaxation.

It’s also possible to change the absorption coefficient differently for the two polarizations. This is called induced dichroism. It also rotates the probe polarization and can also be used to study orientational relaxation.
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!
Semiclassical Nonlinear-Optical Perturbation Theory

- Treat the medium quantum-mechanically and the light classically.
- Assume negligible transfer of population due to the light.
- Assume that collisions are very frequent, but very weak: they yield exponential decay of any coherence.
- Use the density matrix to describe the system. The density matrix is defined according to:
  \[ \rho_{mn} = |m\rangle \langle n| \]
  For any operator A, the mean value is given by: \[ \langle A \rangle = \text{Trace}(\rho A) \]
- Effects that are not included in this approach: saturation, population of other states by spontaneous emission, photon statistics.
The density matrix

If the state of a single two-level atom is:

$$\psi = c_\alpha |\alpha\rangle + c_\beta |\beta\rangle$$

The density matrix, $\rho_{ij}(t)$, is defined as:

$$
\begin{bmatrix}
\rho_{\alpha\alpha} & \rho_{\alpha\beta} \\
\rho_{\beta\alpha} & \rho_{\beta\beta}
\end{bmatrix}
= 
\begin{bmatrix}
c_\alpha^* c_\alpha & c_\alpha^* c_\beta \\
c_\beta^* c_\alpha & c_\beta^* c_\beta
\end{bmatrix}
$$

$\rho_{\alpha\alpha}$ or $\rho_{\beta\beta}$ are the population densities of states $\alpha$ and $\beta$.

$\rho_{\alpha\beta}$ and $\rho_{\beta\alpha}$ are the degree of coherence between states $\alpha$ and $\beta$.

Since excited state populations always eventually decay to ground state populations, $\rho_{ii}$ generally depends on time, $\rho_{ii}(t)$.

And coherence between two states usually decays even faster, so the off-diagonal elements also depends on time.
For a many-atom system, the density matrix, $\rho_{ij}(t)$, is defined as:

$$
\begin{bmatrix}
\rho_{\alpha\alpha}(t) & \rho_{\alpha\beta}(t) \\
\rho_{\beta\alpha}(t) & \rho_{\beta\beta}(t)
\end{bmatrix}
= \begin{bmatrix}
\sum c_\alpha(t)c_\alpha^*(t) & \sum c_\alpha(t)c_\beta^*(t) \\
\sum c_\beta(t)c_\alpha^*(t) & \sum c_\beta(t)c_\beta^*(t)
\end{bmatrix}
$$

where the sums are over all atoms or molecules in the system.

Simplifying:

$$
= \begin{bmatrix}
\sum |c_\alpha(t)|^2 & \sum c_\alpha(t)c_\beta^*(t) \\
\sum c_\beta(t)c_\alpha^*(t) & \sum |c_\beta(t)|^2
\end{bmatrix}
$$

The diagonal elements (gratings) are always positive, while the off-diagonal elements (coherences) can be negative or even complex.

So cancellations can occur in coherences.
Why do coherences decay?

A macroscopic coherence is the sum over all the atoms in the medium.

The collisions "dephase" the emission, causing cancellation of the total emitted light, typically exponentially.
Grating and coherence decay: $T_1$ and $T_2$

A grating or coherence decays as excited states decay back to ground.

A coherence can also cancel out if collisions have randomized the phase of each oscillating atomic dipole.

The time-scales for these decays to occur are always written as:

- **Grating** [$\rho_{\alpha\alpha}(t)$ or $\rho_{\beta\beta}(t)$]: $T_1$ “relaxation time”
- **Coherence** [$\rho_{\alpha\beta}(t)$ or $\rho_{\beta\alpha}(t)$]: $T_2$ “dephasing time”

Collisions cause dephasing but not necessarily de-excitation; therefore, it is generally true that $T_2 \ll T_1$.

The measurement of these times is often the goal of nonlinear spectroscopy!
Nonlinear-Optical Perturbation Theory

The Liouville equation for the density matrix is:

\[ i\hbar \frac{d\rho}{dt} = [V, \rho] \]  

(in the interaction picture)

which can be formally integrated:

\[ \rho(t) = \rho(t_0) + \frac{1}{i\hbar} \int_{t_0}^{t} \left[ V(t'), \rho(t') \right] dt' \]

This can be solved iteratively:

\[ \rho(t) = \sum_{n=0}^{\infty} \rho^{(n)}(t) \]

\[ \rho^{(n)}(t) = \left( \frac{1}{i\hbar} \right)^n \int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 \cdots \int_{t_0}^{\tau_{n-1}} d\tau_n \left[ V(t_1), \left[ V(t_2), \cdots \left[ V(t_n), \rho(t_0) \right] \cdots \right] \right] \]

Note that \( t_0 \leq t_n \leq t_{n-1} \leq \cdots \leq t_1 \leq t \) \( \leftarrow \) i.e., a “time ordering.”
Perturbation Theory (continued)

Expand the commutators in the integrand:

\[
\left[ V(t_1) , [ V(t_2), \ldots [ V(t_n), \rho(t_0) ] \ldots ] \right]
\]

Consider, for example, \( n = 2 \):

\[
\left[ V(t_1) , [ V(t_2), \rho(t_0) ] \right] = \left[ V(t_1), V(t_2) \rho(t_0) - \rho(t_0) V(t_2) \right]
\]

\[
= V(t_1) V(t_2) \rho(t_0) - V(t_1) \rho(t_0) V(t_2) - V(t_2) \rho(t_0) V(t_1) + \rho(t_0) V(t_2) V(t_1)
\]

Thus, \( \rho^{(n)} \) contains \( 2^n \) terms.
Density matrix & Hamiltonian

For an ensemble of 2-level systems in the presence of a laser field:

\[ \frac{\hbar \Omega}{|1\rangle} \quad \frac{\hbar \Omega}{|2\rangle} \]

- population of state \( j = \rho_{jj} \)
- polarization operator \( p \) is:

\[
\begin{bmatrix}
0 & -\mu \\
-\mu & 0
\end{bmatrix}
\]

and so the macroscopic polarization \( P \) is:

\[
P = N \langle p \rangle = N \cdot Tr(\rho p)
\]

\[
= N \cdot Tr\left( \begin{bmatrix}
\rho_{11} & \rho_{12} \\
\rho_{21} & \rho_{22}
\end{bmatrix} \begin{bmatrix}
0 & -\mu \\
-\mu & 0
\end{bmatrix} \right)
\]

\[
= -N\mu(\rho_{12} + \rho_{21})
\]

Hamiltonian \( H = H_0 + H_{\text{int}} \):

\[
H_0 = \begin{bmatrix}
E_1 & 0 \\
0 & E_2
\end{bmatrix} = \begin{bmatrix}
0 & 0 \\
0 & \hbar \Omega
\end{bmatrix}
\]

\[
H_{\text{int}} = p \cdot E = \begin{bmatrix}
0 & -\mu E \\
-\mu E^* & 0
\end{bmatrix}
\]

(we have defined the zero of energy as the energy of state 1)
Diagonal elements of $\rho$

Liouville equation for the diagonal element:

$$i\hbar \frac{\partial \rho_{22}}{\partial t} = \langle 2 [H, \rho] 2 \rangle - i\hbar \frac{\rho_{22} - \rho_{22}^{eq}}{T_1}$$

$$= \langle 2 \begin{bmatrix} 0 & H_{12} \\ H_{21} & \hbar \Omega \end{bmatrix} \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} - \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} \begin{bmatrix} 0 & H_{12} \\ H_{21} & \hbar \Omega \end{bmatrix} \rangle 2 - i\hbar \frac{\rho_{22} - \rho_{22}^{eq}}{T_1}$$

$$= H_{21} \rho_{12} - H_{12} \rho_{21} - i\hbar \frac{\rho_{22} - \rho_{22}^{eq}}{T_1}$$

…and similarly for $\rho_{11}$.

Derive from these an equation for the population difference $\Delta \rho = \rho_{22} - \rho_{11}$

$$i\hbar \frac{\partial \Delta \rho}{\partial t} = 2(H_{21} \rho_{12} - H_{12} \rho_{21}) - i\hbar \frac{\Delta \rho - \Delta \rho_0}{T_1}$$
Off-diagonal elements of $\rho$

Liouville equation for the off-diagonal element:

$$i\hbar \frac{\partial \rho_{12}}{\partial t} = \langle 1 | [H, \rho] | 2 \rangle - i\hbar \frac{\rho_{21}}{T_2}$$

$$i\hbar \frac{\partial \rho_{12}}{\partial t} = -H_{21} \Delta \rho + \left( \hbar \Omega - \frac{i\hbar}{T_2} \right) \rho_{21}$$

Now use the known form for the perturbation:

$$H_{12} = H_{21}^* = -\mu \left( E(t)e^{-i\omega t} - E^*(t)e^{i\omega t} \right)$$

$$\frac{\partial \Delta \rho}{\partial t} = \frac{2i\mu}{\hbar} \left( \rho_{21} + \rho_{12} \right) \left( E^* e^{i\omega t} - E e^{-i\omega t} \right) - \frac{\Delta \rho - \Delta \rho_0}{T_1}$$

$$\frac{\partial \rho_{21}}{\partial t} = \frac{i\mu}{\hbar} \left( E e^{-i\omega t} - E^* e^{i\omega t} \right) \Delta \rho - \left( i\Omega + \frac{1}{T_2} \right) \rho_{21}$$
Rotating wave approximation

\[ \rho_{21}(t) = \sum_n \rho_{21}^{(n)} e^{-i\omega t} \]

\[ \Delta \rho(t) = \sum_m \Delta \rho^{(m)} e^{-i\omega t} \]

Insert into the previous equations, and match terms of like frequency:

\[ \frac{\partial \Delta \rho^{(n)}}{\partial t} = \frac{2i\mu}{\hbar} \left( \rho_{21}^{(n-1)} E^* - \rho_{21}^{*(n-1)} E \right) - \frac{\Delta \rho^{(n)} - \Delta \rho^{(n)}}{T_1} \]

\[ \frac{\partial \rho_{21}^{(n)}}{\partial t} = A \rho_{21}^{(n)} + \frac{i\mu}{\hbar} E \Delta \rho^{(n-1)} \]

\[ A = -\frac{1}{T_2} - i(\Omega - \omega) \]

which can be integrated to yield:

\[ \Delta \rho^{(n)} = \int_{-\infty}^{t} dt' \left( \frac{2i\mu}{\hbar} \left( \rho_{21}^{(n-1)} E^* (t') - \rho_{21}^{*(n-1)} E(t') \right) \right) \exp \left[ \frac{t' - t}{T_1} \right] \]

\[ \rho_{21}^{(n)} = \int_{-\infty}^{t} dt' \left( \frac{i\mu}{\hbar} E(t') \Delta \rho^{(n-1)} \right) \exp \left[ \int_{t'}^{t} A dt'' \right] \]
Iterative method for solving perturbatively

We have a system of equations of the form:

\[
\Delta \rho^{(n)} = F(\rho^{(n-1)}_{21}) \\
\rho^{(n)}_{21} = G(\Delta \rho^{(n-1)})
\]

Start with \( \rho^{(0)}_{21} = 0 \) and \( \Delta \rho^{(0)} = \rho_0 \) and iterate:

\[
\rho^{(1)}_{21} = G(\Delta \rho^{(0)}) \quad \rightarrow \quad \Delta \rho^{(2)} = F(\rho^{(1)}_{21}) = F(G(\Delta \rho^{(0)})) \\
\quad \rightarrow \quad \rho^{(3)}_{21} = G(\Delta \rho^{(2)}) = G(F(G(\Delta \rho^{(0)})))
\]

\( \rho^{(3)}_{21} \) term looks like:

\[
\rho^{(3)}_{21} = -2i\rho_0 \left( \frac{\mu}{\hbar} \right)^3 \int_{-\infty}^{t} \int_{-\infty}^{t_1} \int_{-\infty}^{t_2} \int_{-\infty}^{t_3} \exp \left[ \frac{t_2 - t_1}{T_1} + \int_{t_1}^{t} \text{Adt'} \right] \times \\
\left\{ E(t_1) E^*(t_2) E(t_3) \exp \left[ \int_{t_3}^{t_2} \text{Adt'} \right] + E(t_1) E(t_2) E^*(t_3) \exp \left[ \int_{t_3}^{t_2} A^* \text{dt'} \right] \right\}
\]

Must be a \( \chi^{(3)} \) process!
Multiple pulses

\[ \rho_{21}^{(3)} = -2i\rho_0 \left( \frac{\mu}{\hbar} \right)^3 \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t} dt_2 \int_{-\infty}^{t} dt_3 \exp \left[ \frac{t_2 - t_1}{T_1} + \int_{t_1}^{t} A dt' \right] \times \]

\[ \left\{ \begin{aligned} & E(t_1)E^*(t_2)E(t_3)\exp \left[ \int_{t_3}^{t_2} A dt' \right] + E(t_1)E(t_2)E^*(t_3)\exp \left[ \int_{t_3}^{t_2} A^* dt' \right] \end{aligned} \right\} \]

Suppose there are two pulses, both short compared to all relevant time scales:

\[ E(t) = E_1 \delta(t) e^{ik_1r} + E_2 \delta(t - \tau) e^{ik_2r} \]

A product of three of these \( E(t) \) fields gives 8 terms, each with one of these four wave vectors:

\[ k_1 + k_2 - k_2 \quad k_1 + k_2 - k_1 \quad k_1 + k_1 - k_2 \quad k_2 + k_2 - k_1 \]

phase matching, of a sort: pick the direction you care about
Example: application to the two-pulse echo

Choose the $2k_1 - k_2$ direction.

Then only two terms (of 16 in $\rho_{21}^{(3)}$) contribute:

$$
\rho_{21}^{(3)} = -2i\rho_0 E_1^2 E_2 \left( \frac{\mu}{\hbar} \right)^3 \int_{-\infty}^{t} \int_{-\infty}^{t_1} \int_{-\infty}^{t_2} \exp \left[ \frac{t_2 - t_1}{T_1} + \int_{t_1}^{t} A dt' \right] \times 
\left\{ \delta(t_1) \delta(t_2 - \tau) \delta(t_3) \exp \left[ \int_{t_3}^{t_2} A dt' \right] + \delta(t_1) \delta(t_2) \delta(t_3 - \tau) \exp \left[ \int_{t_3}^{t_2} A^* dt' \right] \right\}
$$

First term: must have $t_2 \geq 0$ AND $t_2 = \tau \quad \rightarrow \quad \tau \geq 0$

must have $t_1 \geq \tau$ AND $t_1 = 0 \quad \rightarrow \quad \tau \leq 0$

signal only for $\tau = 0$

"coherent spike"

Second term: must have $\tau < 0$ and $t > 0$ (no other constraints); it gives rise to signal at values of $\tau$ other than merely $\tau = 0$
Example: application to the two-pulse echo

Homogeneous broadening

Polarization = \( N \mu \rho_{21} \sim \exp\left[(-t + \tau)/T_2'\right] \)

measured signal \( S(\tau) \):

\[
S(\tau) = \int \left| P^{(3)} \right|^2 dt \propto \begin{cases} 
  e^{\frac{2\tau}{T_2'}} & \text{for } \tau < 0 \\
  0 & \text{otherwise} 
\end{cases}
\]

where \( \frac{1}{T_2'} = \frac{1}{T_1} + \frac{1}{T_2} \)

Inhomogeneous broadening

We must integrate over the inhomogeneous distribution \( g(\Delta\omega) \):

\[
P^{(3)} \propto \int d(\Delta\omega) g(\Delta\omega) \rho^{(3)}_{21}
\]

\[
\sim e^{(-t+\tau)/T_2} \int d(\Delta\omega) e^{-i\Delta\omega(t+\tau)} g(\Delta\omega) \delta(t+\tau)
\]

\( P^{(3)} \) is non-zero only at \( t = -\tau \)

\[
S(\tau) \propto \int_0^\infty \left| P^{(3)} \right|^2 dt = e^{2\tau/T_2} \int_0^\infty dt e^{-2\tau/T_2} \delta(t+\tau)
\]

\[
S(\tau) \propto \begin{cases} 
  e^{4\tau/T_2} & \text{for } \tau < 0 \\
  0 & \text{otherwise} 
\end{cases}
\]
**Echo vs. FID: can we tell?**

**Homogeneous case:** phase-matched free-induction decay

- Pulse #1
- Pulse #2

Free-induction decay: $2k_1 - k_2$

**Inhomogeneous case:** photon echo

- Pulse #1
- Pulse #2

Echo

It can be difficult to distinguish between these two cases experimentally!
Echo vs. FID: how to tell

One way to distinguish:

FWM upconversion using a third optical pulse

e.g., M. Mycek et al., Appl. Phys. Lett., 1992
Photon echo: what’s going on?

The pseudo-vector:
- $z$ component denote population state
- $xy$ components denote polarization state

The photon echo is physically equivalent to the “spin echo” in NMR spectroscopy, except for the extra complication of wave-vector phase matching ($2k_2 - k_1$)