# Ultrafast Laser Spectroscopy techniques

How do we do ultrafast laser spectroscopy?

Generic ultrafast spectroscopy experiment

The pump-probe experiment

Lock-in detection

Transient-grating spectroscopy

Ultrafast polarization spectroscopy



Spectrally resolved pump-probe spectroscopy

Theory of ultrafast measurements: the Liouville equation

Iterative solution

# **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 pump 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 determine!), so the absorption and refractive index eventually return to their initial (before excitation) values.

# The simplest ultrafast spectroscopy method is the Pump-Probe technique.



The pump and probe pulses can be the same or different colors.

## **Modeling pump-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:

$$\Delta \alpha(\tau) = \Delta \alpha_0 \exp(-\tau/T_1)$$
 for  $\tau > 0$ 

where  $\tau$  is the delay after excitation, and  $T_I$  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,  $T_1$ :

$$I_{transmitted} (\tau) = I_{incident} \exp\left[-\left(\alpha_0 - \Delta \alpha e^{-\tau/T_1}\right)L\right] \text{ where } L = \text{sample length}$$
$$= I_{incident} e^{-\alpha_0 L} \exp\left[\Delta \alpha e^{-\tau/T_1}L\right]$$

 $\approx I_{incident} e^{-\alpha_0 L} \left[ 1 + \Delta \alpha e^{-\tau/T_1} L \right]$  assuming  $\Delta \alpha_0 L \ll 1$ 

# Modeling pumpprobe measurements (cont'd)

$$I_{transmitted} (\tau) \approx I_{incident} e^{-\alpha_0 L} \left[ 1 + \Delta \alpha e^{-\tau/T_1} L \right]$$

This is the transmitted probe intensity before the pump pulse arrives at  $\tau = 0$ .

$$I_{transmitted} \left( \tau \right) \approx I_{transmitted} \left( 0^{-} \right) \left[ 1 + \Delta \alpha e^{-\tau/T_{1}} L \right]$$

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

$$\Delta T(\tau) / T_0 \equiv \left[ I_{transmitted}(\tau) - I_{transmitted}(0^{-}) \right] / I_{transmitted}(0^{-})$$

where we've divided the numerator and denominator by the incident intensity to obtain transmissivities at  $\tau$  and 0.

 $\Rightarrow$ 

$$\Delta T(\tau) / T_0 \approx \Delta \alpha_0 \exp(-\tau / T_l) L$$



## More complex pump-probe measurements



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:



# **Lock-in Detection** greatly increases the sensitivity in pump-probe experiments.

This involves **chopping** the pump pulse at a given frequency and detecting at that frequency with a lock-in detector:



Lock-in detection automatically subtracts off the transmitted power in the absence of the pump pulse. With high-rep-rate lasers, it increases sensitivity by several orders of magnitude!

# Pump-probe studies of bacterio-rhodopsin

Rhodopsin is the main molecule involved in vision. After absorbing a photon, rhodopsin undergoes a manystep 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!

# Pump-probe measurements of Hypericin, an anti-viral substance

When excited by light, Hypericin deactivates HIV. So it would be nice to understand how it works.



These curves (for two different solvents) show the rise time for a proton-transfer process important in its biological activity.

# **Pump-probe reflection spectroscopy**

Exciting a surface and probing its reflectivity at a later delay can reveals surface physics.

Here, a **quantum wire** is studied using ultrashort pulses in a **near-field scanning optical microscope** to yield 200nm spatial resolution, too!





 $\Delta R/R$  vs. x and y for a delay of 10ps

Emiliani, et al., Ultrafast Phenomena XII, p. 256 (2000).

# Multiple-wavelength ultrafast absorption It's often helpful to perform experiments

It's often helpful to perform experiment for multiple probe wavelengths.



#### Buckminster-fullerene

Electron transfer from a polymer to a buckyball is very fast.

It has applications to photo-voltaics, nonlinear optics, and artificial photosynthesis.

Brabec, et al., Ultrafast Phenomena XII, p. 589 (2000).

# Pump-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 pump-probe data.

# Pump-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.

Zadoyan, et al., Ultrafast Phenomena X, p. 194 (1996).

#### 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. This signal is called the **coherence spike** or **coherent artifact**. Sometimes you see it; sometimes you don't.



# Taking advantage of the induced grating: the Transient-Grating Technique.

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



Diffracted

Delay, τ

 $\cap$ 

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 pump-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 pump pulses and which is the probe pulse? Pump pulse

#1 (acting as

the probe)

Pump pulse #2

#### Intensity fringes in sample due to a pump pulse and the probe acting as another pump pulse

Delay  $\downarrow$  Probe pulse (acting as a pump pulse) A transient-grating experiment with a coherence spike: 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:

$$\eta(\tau) \approx \left(\frac{\Delta \alpha(\tau)L}{4}\right)^2 + \left(\frac{\Delta n(\tau)kL}{2}\right)^2 \text{ Refractive index (amplitude)}$$

$$f = \int_{\text{grating}} \frac{\Delta \alpha(\tau)L}{4} + \left(\frac{\Delta n(\tau)kL}{2}\right)^2 \text{ Refractive index (phase) grating}$$

This is in contrast to the pump-probe technique, which is only sensitive to the change in absorption and depends on it linearly.

If the absorption grating dominates and the pump-probe decay is  $\exp(-\tau/T_1)$ , then the TG decay will be  $\exp(-2\tau/T_1)$ :

H. Eichler, *Laser-Induced Dynamic Gratings*, Springer-Verlag, 1986.



## Another technique: 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 (if the decay is slow) or, by time-gating it



# Time-resolved fluorescence decay

The molecule trans-azobenzene (dissolved in hexane) emits fluorescence after fsec excitation in the UV (280 nm). This fluorescence changes as the molecule isomerizes on a picosecond time scale.



Fujino et al., J. Phys. Chem. A (2001) The isomerization pathways can be assigned from measurements of the timeresolved fluorescence data at several different wavelengths.



# **Ultrafast Polarization Spectroscopy**

A 45°-polarized pump 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.



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.

# Ultrafast spectroscopy setups are becoming more and more sophisticated!

Spatial Light Modulator Driven Coherent Multi-Dimensional Spectroscopy

A tool for studying electron coupling and dynamics in condensed matter systems, including semiconductor nanostructures and biological light harvesting complexes.

Jonathan Tollerud, Christopher Hall, Jeffrey Davis



# 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. The range of techniques is enormous, and growing all the time.

# Modeling ultrafast experiments: Semiclassical Nonlinear-Optical Perturbation Theory

- Treat the medium quantum-mechanically and the light classically.
- Assume negligible transfer of population due to the light: it is a perturbation.
- 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:  $\rho_{mn} = |m\rangle \langle n|$  (using bra & ket notation)

For any operator A, the mean value is given by:  $\langle A \rangle = Trace(\rho A)$ 

• Various effects 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:



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

 $(\mathbf{0})$ 

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.

### The density matrix for a many-atom system

For a many atom system, the density matrix,  $\rho_{ii}(t)$ , 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 (populations) 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.



One reason is that excited states decay back to the ground state.

#### Here's another reason:

Collisions can "dephase" the emission, causing cancellation and gradual decay of the total coherence, even if the excited state population is unchanged.

# Grating and coherence decay: $T_1$ and $T_2$

A population 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.

It is usually assumed that both of these decays occur exponentially in time, so that each process has a single time constant. By convention, these are always written as:

Population [ $\rho_{\alpha\alpha}(t)$  or  $\rho_{\beta\beta}(t)$ ]:  $T_1$  "relaxation time"

Coherence  $[\rho_{\alpha}(t) \text{ or } \rho_{\alpha}(t)]$ :  $T_2$  "dephasing time"

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

The measurement of these times is often the goal of nonlinear spectroscopy!

## **Evolution of the density matrix**

The Liouville equation for the evolution of a mixed state (described by a density matrix) is:

 $i\hbar \frac{d\rho}{dt} = [H, \rho]$  where *H* is the system Hamiltonian.

This equation does not include energy relaxation or the effects of collisions. So we generally need to add in those effects in an *ad hoc* way, to account for both population  $(T_1)$  and coherence  $(T_2)$  decay.

For a 2-level system, the Hamiltonian is a 2x2 matrix:

$$\hbar \Omega \left\{ \begin{array}{ccc} |2\rangle \\ & H_0 = \begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix} = \begin{bmatrix} 0 & 0 \\ 0 & \hbar \Omega \end{bmatrix} \right.$$

where this last step has defined the zero of energy as the energy of state 1

### **Density matrix & the Polarization**

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

 $\hbar \Omega \left\{ \begin{array}{c|c} \hbar \omega_{laser} & |2\rangle \\ & |1\rangle \end{array} \right.$  The polarization operator *p* is:  $p = \begin{bmatrix} 0 & -\mu \\ -\mu & 0 \end{bmatrix}$ 

where  $\boldsymbol{\mu}$  is the dipole transition moment between the two states:

$$\mu = e \int \psi_2^*(r) r \psi_1(r) d^3 r = e \langle 2|r|1 \rangle$$

and so the macroscopic polarization *P* is:

$$P = N \langle p \rangle = N \cdot Tr(\rho p) = N \cdot Tr \left\{ \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} \begin{bmatrix} 0 & -\mu \\ -\mu & 0 \end{bmatrix} \right\}$$
$$= -N\mu(\rho_{12} + \rho_{21})$$

The polarization is determined by the off-diagonal elements of the density matrix. And their time evolution is computed using the Liouville equation.

### **Density matrix & Hamiltonian**

The Hamiltonian consists of two pieces: the unperturbed twolevel system, plus the interaction (perturbation) term describing the light-matter interaction.

 $H = H_0 + H_{int} \text{ where:}$   $H_0 = \begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix} = \begin{bmatrix} 0 & 0 \\ 0 & \hbar\Omega \end{bmatrix} \qquad H_{int} = p \cdot E = \begin{bmatrix} 0 & -\mu E \\ -\mu E^* & 0 \end{bmatrix}$   $H = \begin{bmatrix} 0 & -\mu E \\ -\mu E^* & \hbar\Omega \end{bmatrix}$ 

Thus the Liouville equation  $i\hbar \frac{d\rho}{dt} = [H, \rho]$ , becomes:

$$i\hbar\frac{d}{dt}\begin{bmatrix}\rho_{11} & \rho_{12}\\\rho_{21} & \rho_{22}\end{bmatrix} = \begin{bmatrix}0 & -\mu E\\-\mu E^* & \hbar\Omega\end{bmatrix}\begin{bmatrix}\rho_{11} & \rho_{12}\\\rho_{21} & \rho_{22}\end{bmatrix} - \begin{bmatrix}\rho_{11} & \rho_{12}\\\rho_{21} & \rho_{22}\end{bmatrix}\begin{bmatrix}0 & -\mu E\\-\mu E^* & \hbar\Omega\end{bmatrix}$$

### **Diagonal elements of** $\rho$

We know that excited state populations typically decay exponentially to their equilibrium value, with a time constant  $T_1$ . So let's insert that term:

Liouville equation for the  $\rho_{22}$  element:

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

$$2 \left[ \begin{bmatrix} 0 & -\mu E \\ -\mu E^* & \hbar \Omega \end{bmatrix} \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} - \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} \begin{bmatrix} 0 & -\mu E \\ -\mu E^* & \hbar \Omega \end{bmatrix} | 2 \rangle - i\hbar \frac{\rho_{22} - \rho_{22}^{eq}}{T_1}$$

$$= -\left( \mu E^* \rho_{12} + \mu E \rho_{21} \right) - i\hbar \frac{\rho_{22} - \rho_{22}^{eq}}{T_1}$$

...and we could work out a similar expression for  $\rho_{11}$ .

### **Diagonal elements of** $\rho$

From these results, we derive an equation for the population difference  $\Delta \rho = \rho_{22} - \rho_{11}$ :

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

Here,  $\Delta \rho_0$  is the equilibrium population difference (which need not be zero for finite temperature).

This shows that the time evolution of the **population difference** depends on the off-diagonal elements, i.e., the **polarization**!

What about the time evolution of the off-diagonal elements?

# **Off-diagonal elements of** $\rho$

As with the population terms, the coherence terms also decay, but with a different time constant,  $T_2$ . We need to also insert this one by hand. We assume that, in the equilibrium state, there is zero coherence between the two states.

Liouville equation for the off-diagonal element:

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

Using the same matrices as before for  ${\rm H}$  and  $\rho,$  we find that this is:

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

The time evolution of  $\rho_{21}$  depends on  $\Delta \rho$ !

### A system of equations for the evolution of $\rho$

We have found two coupled equations for  $\rho_{21}$  and  $\Delta \rho$ :

$$\frac{\partial \Delta \rho}{\partial t} = \frac{2i\mu}{\hbar} (\rho_{21} + \rho_{12}) (E^* e^{i\omega t} - E e^{-i\omega t}) - \frac{\Delta \rho - \Delta \rho_0}{T_1}$$
$$\frac{\partial \rho_{21}}{\partial t} = \frac{i\mu}{\hbar} (E e^{-i\omega t} - E^* e^{i\omega t}) \Delta \rho - \left(i\Omega + \frac{1}{T_2}\right) \rho_{21}$$

To simplify this system of equations, we use the rotating wave approximation (RWA), which assumes that both  $\rho_{21}$  and  $\Delta\rho$  can be written as sums of harmonics of the driving (laser) frequency:

$$\rho_{21}(t) = \sum_{n} \rho_{21}^{(n)} e^{-in\omega t}$$
$$\Delta \rho(t) = \sum_{m} \Delta \rho^{(m)} e^{-im\omega t}$$

We can insert these assumed forms into the above equations, and match up terms with the same frequency exponents.

### **Rotating wave approximation**

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

$$\frac{\partial \Delta \rho^{(n)}}{\partial t} = \frac{2i\mu}{\hbar} \left( \rho_{21}^{(n-1)} E^* - \rho_{21}^{*(n-1)} E \right) - \frac{\Delta \rho^{(n)} - \Delta \rho_0^{(n)}}{T_1}$$
$$\frac{\partial \rho_{21}^{(n)}}{\partial t} = \Gamma \rho_{21}^{(n)} + \frac{i\mu}{\hbar} E \Delta \rho^{(n-1)} \qquad \text{where we have defined} \\ a \text{ shorthand notation:} \quad \Gamma = -\frac{1}{T_2} - i(\Omega - \omega_{Laser})$$

These can be integrated to yield:

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

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

# Iterative method for solving perturbatively

We have a system of equations of the form:

$$\Delta \rho^{(n)} = F(\rho_{21}^{(n-1)})$$
$$\rho_{21}^{(n)} = G(\Delta \rho^{(n-1)})$$

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

$$\rho_{21}^{(1)} = G\left(\Delta\rho^{(0)}\right) \longrightarrow \Delta\rho^{(2)} = F\left(\rho_{21}^{(1)}\right) = F\left(G\left(\Delta\rho^{(0)}\right)\right)$$
$$\longrightarrow \rho_{21}^{(3)} = G\left(\Delta\rho^{(2)}\right) = G\left(F\left(G\left(\Delta\rho^{(0)}\right)\right)\right)$$

Implementing this procedure, the  $\rho_{21}^{(3)}$  term looks like this:

$$\rho_{21}^{(3)} = -2i\rho_0 \left(\frac{\mu}{\hbar}\right)^3 \int_{-\infty}^t dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 \exp\left[\frac{t_2 - t_1}{T_1} + \int_{t_1}^t \Gamma dt'\right] \times \left\{ E(t_1)E^*(t_2)E(t_3)\exp\left[\int_{t_3}^{t_2} \Gamma dt'\right] + E(t_1)E(t_2)E^*(t_3)\exp\left[\int_{t_3}^{t_2} \Gamma^* dt'\right] \right\}$$

Proportional to the product of three E fields: it must describe a  $\chi^{(3)}$  process!

### **Multiple pulses**

$$\rho_{21}^{(3)} = -2i\rho_0 \left(\frac{\mu}{\hbar}\right)^3 \int_{-\infty}^t dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 \exp\left[\frac{t_2 - t_1}{T_1} + \int_{t_1}^t \Gamma dt'\right] \times \left\{ E(t_1)E^*(t_2)E(t_3)\exp\left[\int_{t_3}^{t_2} \Gamma dt'\right] + E(t_1)E(t_2)E^*(t_3)\exp\left[\int_{t_3}^{t_2} \Gamma^* dt'\right] \right\}$$

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



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

$$k_1 + k_2 - k_2$$
  $k_1 + k_2 - k_1$   $k_1 + k_1 - k_2$   $k_2 + k_2 - k_1$ 

phase matching: pick the direction you care about

## **Example: the coherent diffraction direction**

 $K_2$ 

2k<sub>1</sub>

Choose the wave vector  $2k_1 - k_2$ .

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

$$-\mathbf{k}_{2} \quad \rho_{21}^{(3)} = -2i\rho_{0}E_{1}^{2}E_{2}\left(\frac{\mu}{\hbar}\right)^{3}\int_{-\infty}^{t}dt_{1}\int_{-\infty}^{t_{1}}dt_{2}\int_{-\infty}^{t_{2}}dt_{3} \exp\left[\frac{t_{2}-t_{1}}{T_{1}}+\int_{t_{1}}^{t}\Gamma dt'\right] \times \\ \left\{\delta(t_{1})\delta(t_{2}-\tau)\delta(t_{3})\exp\left[\int_{t_{3}}^{t_{2}}\Gamma dt'\right]+\delta(t_{1})\delta(t_{2})\delta(t_{3}-\tau)\exp\left[\int_{t_{3}}^{t_{2}}\Gamma^{*}dt'\right]\right\}$$

First term: must have  $t_2 \ge 0$  AND  $t_2 = \tau$   $\longrightarrow \tau \ge 0$  signal only must have  $t_1 \ge \tau$  AND  $t_1 = 0$   $\longrightarrow \tau \le 0$  for  $\tau = 0$ 

"coherence 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  $\tau = 0$