Linear and nonlinear spectroscopy

We've seen that we can determine molecular frequencies and dephasing rates (for electronic, vibrational, or spin degrees of freedom) from frequency-domain or time-domain measurements whose results are related through FT. In general:

Parameter	Time Domain S(t)	Frequency Domain S(ω)
Large ω_0	Fast oscillations	High frequency
Small ω_0	Slow oscillations	Low frequency
Large γ	Fast decay	Broad linewidth
Small γ	Slow decay	Narrow linewidth

The FT relations obtain for the light field itself as well as the material responses to it. Short pulses of light have broad spectral widths.

Dephasing rate γ can have very different origins.

Damping – the energy decays back to zero – rate γ_1, time $T_1 = 1/\gamma_1$
"Pure" dephasing – energy is retained, oscillation phase is lost – rate $\gamma_2{}^*$, time $T_2{}^* = 1/\gamma_2{}^*$
    ($T_2{}^*$ notational convention is from NMR)
Inhomogeneous dephasing – energy is retained, and oscillations stay in phase on any individual molecule, but oscillations on different molecules go out of sync – rate γ_3, time $T_3 = 1/\gamma_3$. Sometimes inhomogeneous dephasing rate (or inhomogeneous linewidth) is labeled "Δ."
Total dephasing rate is sum of all three contributions: $\gamma = \gamma_1 + \gamma_2{}^* + \gamma_3$
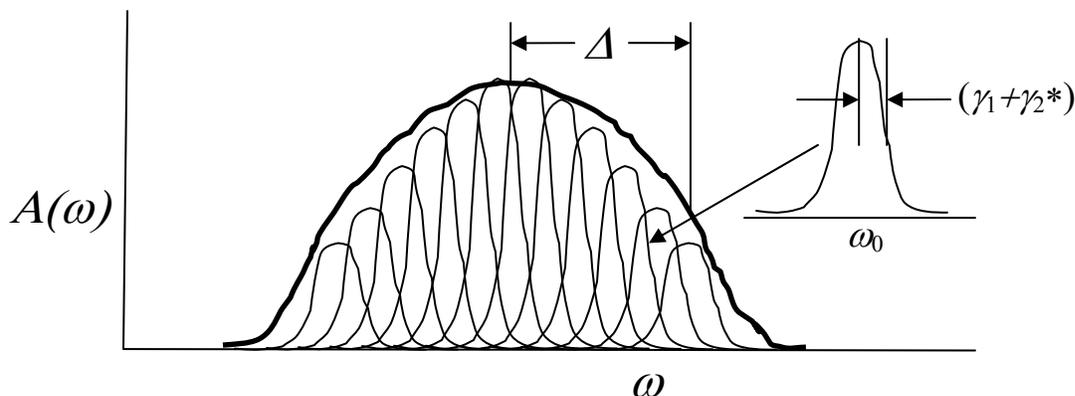
This can happen if different local molecular environments cause different local resonance frequencies ω_0.

How can we distinguish the different contributions??
In "linear" spectroscopy – where the sample response is linearly proportional to the EM field – we cannot!
But there are many "nonlinear" spectroscopies that make it possible.
Nonlinear spectroscopy: sample response is a *nonlinear* function of the driving field

<u>Time-resolved "pump-probe" measurements</u> – measure γ_1
An excitation or "pump" light pulse makes excited states. They may dephase quickly, but the energy is still there in excited molecules that are not oscillating coherently anymore. A variably delayed "probe" pulse can be used to monitor the excited-state population and its decay to the ground state.
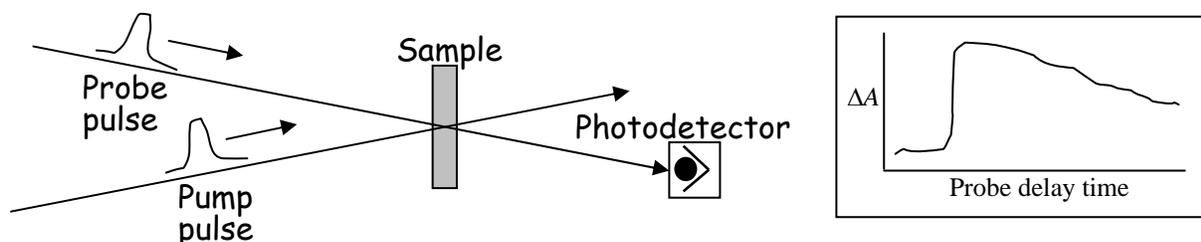

This can be done on femtosecond, picosecond, nanosecond,..., many-second time scales. The probe pulse absorption is changed by the pump pulse because the excited states and ground states absorb differently.

<u>Time-resolved fluorescence</u>
Sometimes the excited molecules return to the ground state by <u>fluorescence</u> – they emit a photon. Unlike absorption, which can be described classically or quantum mechanically, fluorescence is purely quantum mechanical! That's because the excited molecule just spontaneously emits the photon – there's no driving force acting on it.

Fluorescence
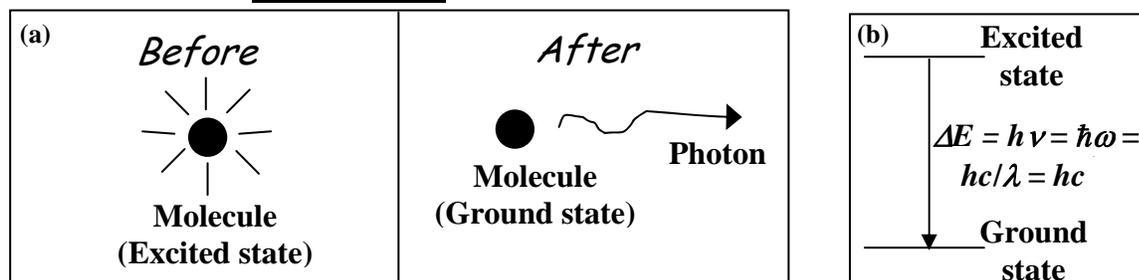
Time-resolved fluorescence measurement

3.2
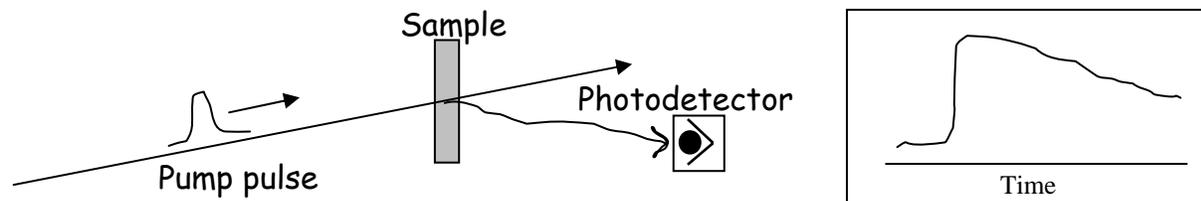
Fluorescence emerges in all directions. Some reaches the photodetector, producing a signal whose time-dependence is measured. As the excited molecules return to the ground state, the amount of fluorescence decreases.

You'll make measurements of fluorescence, but not time-resolved. The fluorescence spectrum reveals excited-state energy levels, similar to the absorption spectrum.

In many cases, molecules or materials lose their energy non-radiatively, heating up their surroundings. Either way, the time for relaxation back to the ground state is T_1. It measures how long it takes for energy to leave the molecules.

Other contributions to total dephasing rate:
NMR "spin echo" measurements can determine the amount of inhomogeneous dephasing. Inhomogeneous dephasing is due to variation (inhomogeneity) in the surroundings of different molecules that lead to slight shifts in their resonant frequencies.

First an RF pulse flips the spins by 90 degrees (a "$\pi/2$" pulse), aligning them along the x axis. Then they start to precess – but not all at exactly the same frequency! So some run ahead of the pack, and some behind.

Then another RF pulse comes a certain time, τ, later, and flips the spins 180 degrees (a "π" pulse), keeping them in the xy plane but reversing their directions – so the fast ones find themselves trailing the pack and the slow ones find themselves leading! And after another time period τ they are all re-phased! This produces a signal, just like before they went out of phase. And this is measured. So the inhomogeneous dephasing is removed!

Spin echo measurement
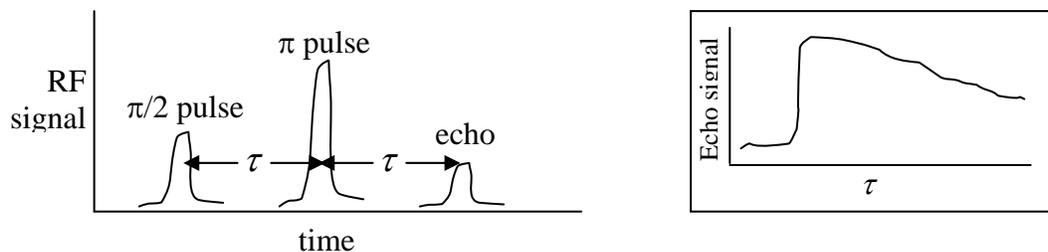
If the time interval τ is increased, the signal still decays due to lifetime (T_1), which in the spin case means the spins lose their net alignments in the xy-plane. The signal also decays due to "pure" dephasing: the molecules still have their excited-state energy (i.e. the spins are still aligned in the xy-plane) but they no longer oscillate phase-coherently – not just

3.3

out of sync with each other, but no longer coherent relative to their own oscillations at the beginning.

If the lifetime also is determined in a pump-probe measurement, then the "pure" dephasing can also be determined.

"Photon echo" measurements can be used to determine vibrational or electronic inhomogeneous dephasing rates.

A similar measurement can be made except with the π pulse first, then $\pi/2$. The first pulse delicately places the system in the higher spin level, without any coherent spin oscillations, by exactly reversing the initial magnetization. The second pulse takes the system from there to the xy plane, where precession leads to oscillating signal. After the first pulse, the system can relax back down to the ground state (the initial spin level) – this is energy relaxation, at the rate γ_1 given by the lifetime T_1. So if you delay the second pulse, the oscillating signal strength decreases at that rate, which can be measured!

5.35 / 5.35U Introduction to Experimental Chemistry
Fall 2012