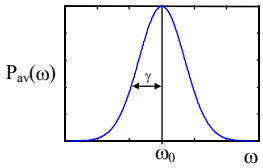
Frequency- and Time-Domain Spectroscopy

We just showed that you could characterize a system by taking an absorption spectrum. We select a frequency component using a grating or prism, irradiate the sample, and measure how much gets absorbed we just change frequency and repeat.

(1) Absorption Spectrum ↔ Frequency domain



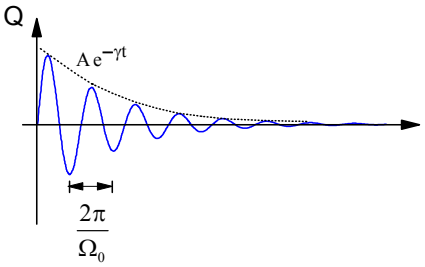
Vary frequency of driving field.

Disperse color → measure power absorbed

The variables ω_0 and γ characterize the time-dependent behavior of our H.O.

So we could also measure these variables if we applied a short driving force and watched the coordinate directly.

(2) Watch coordinate ↔ Time domain



short driving force → watch relaxation/oscillation

$$F_{ext} = F_0\,\delta(t) \quad \rightarrow \quad Q(t) = \frac{F_0}{m} e^{-\gamma t} \sin \Omega_0 t$$

This is the basis for time-resolved spectroscopy using short pulses of light to exert an impulse reponse on the system and watch chemical processes happen.

Also, all modern NMR instruments work this way, applying a burst of RF radiation to sample in field and watch relax.

The information content is essentially the same in either domain. Why use time?

1) All data collected in single observation—faster than collecting one frequency point at a time!

2) Resolving power between peaks is often better.

In practice, different methods work better for different spectroscopic or different types of measurements/information.

Fourier Transform Relations

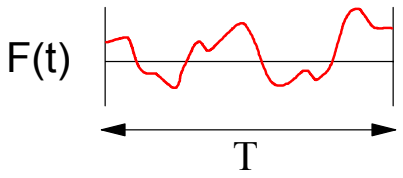
In fact, there is a formal relationship between the time domain and frequency domain

→ **Fourier transform**:

Joseph Fourier showed that any periodic function can be expressed as an expansion in cosines + sines.

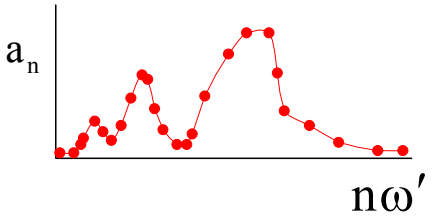
$$F(t) = \sum_{n=1}^{\infty} \left[a_n \cos(n\omega' t) + b_n \sin(n\omega' t) \right]$$

ω' : base frequency



$$\omega' = \pi / T$$

So we can either represent data as the time response, or the value of all of the expansion coefficients in freq. → the spectrum!



For continuous functions, these are related through the Fourier Transform integrals:

$$\textit{Time domain}\ \ S(t) \quad \leftrightarrow \quad \textit{Frequency domain}\ \ S(\omega)$$

$$S(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} S(\omega) \sin \omega t \, d\omega \quad \leftrightarrow \quad S(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} S(t) \sin \omega t \, dt$$

(this gives $S(t)$ if we know $S(\omega)$) (this gives $S(\omega)$ if we know $S(t)$)

For our harmonic oscillator we find:

$$S(t) \propto e^{-\gamma t} \sin \omega_0 t \quad \leftrightarrow \quad S(\omega) \propto \frac{\gamma}{(\omega - \omega_0)^2 + \gamma^2}$$

Parameters in the time and frequency domains:

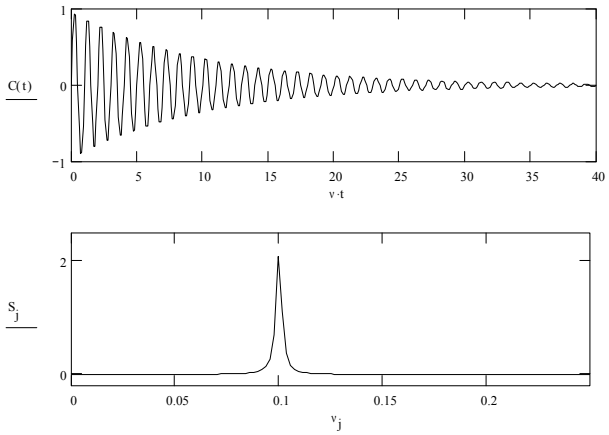
Parameter	Time Domain S(t)	Frequency Domain S(ω)
Large ω_0	Fast oscillations	High frequency
Small ω_0	Slow oscillations	Low frequency
Large γ	Fast decay	Broad linewidth
Small γ	Slow decay	Narrow linewidth

Examples of Fourier Transforms

1) $C(t) = e^{-\gamma t}\sin(\omega t)$ with $\omega/2\pi = \nu = 0.1$ and $\gamma = 0.01$

(The units of time or frequency are arbitrary – lets call it seconds. The time period for oscillation $1/\nu = 10$ sec and the time scale for relaxation is $1/\gamma = 100$ sec)

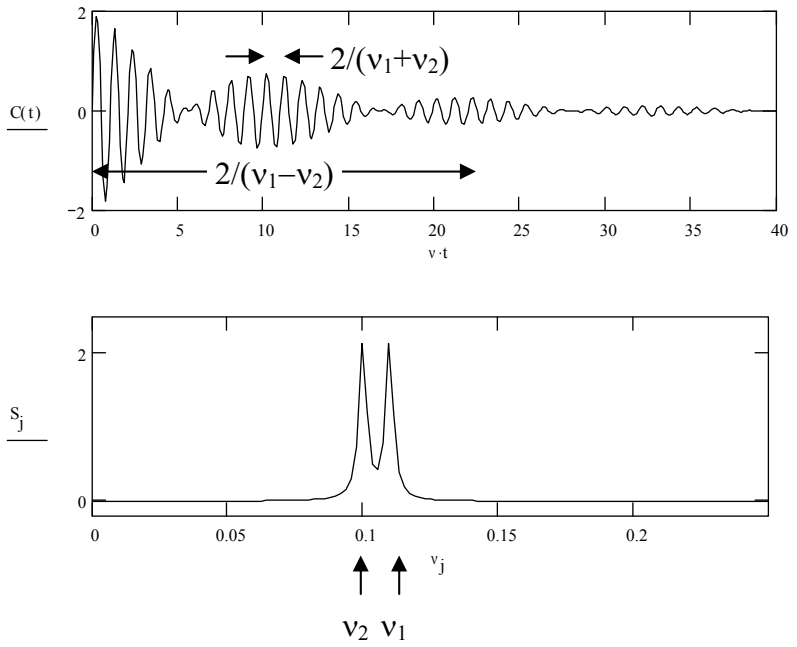
S is the Fourier transform of C(t):



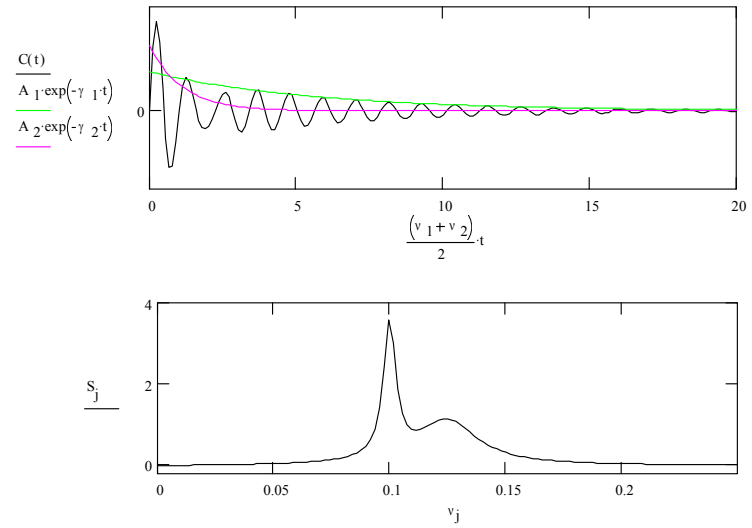
2) If we have two superimposed oscillations: $C(t) = e^{-\gamma t}\sin(\omega_1 t) + e^{-\gamma t}\sin(\omega_2 t)$

with $\omega_1/2\pi = \nu_1 = 0.1$; $\omega_2/2\pi = \nu_2 = 0.11$; and $\gamma = 0.01$

then we expect two peaks in the spectrum at the two frequencies, each with linewidth 2γ.
In time, this manifests itself as two beat frequencies. One with a time period corresponding to the mean frequency $(\nu_1+\nu_2)/2$, and the other to the frequency splitting $(\nu_1-\nu_2)/2$.

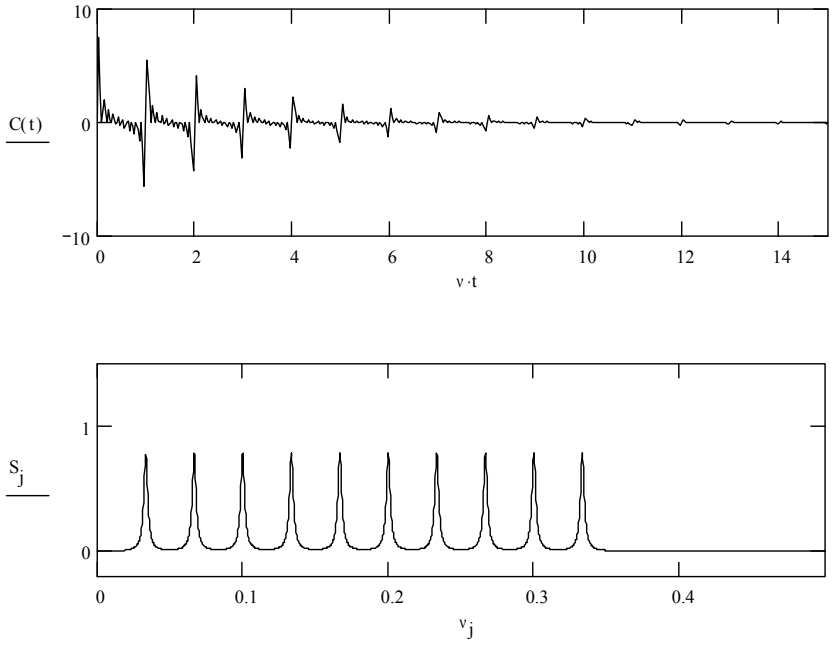


3) Two superimposed oscillations: $C(t) = A_1 \exp(-\gamma_1 t)\sin(\omega_1 t) + A_2 \exp(-\gamma_2 t)\sin(\omega_2 t)$
with $\omega_1/2\pi = \nu_1 = 0.1$; $\omega_2/2\pi = \nu_2 = 0.125$; $\gamma_1 = 1/50$; $\gamma_2 = 1/10$; $A_1 = 3$; $A_2 = 5$.



4) A sum of harmonics in ω: $C(t) = \sum_{n=1}^{10} \exp(-\gamma t)\sin(n\,\omega t)$ with $\omega/2\pi = \nu = 0.03$ and $\gamma = 0.01$.

These are similar to what you will see in rotational and rotational-vibrational spectra. A regularly spaced set of absorption features represent a behavior in time, where all frequencies constructively interfere at periodic multiples of the fundamental period (recurrences).



Damping

Time-dependent process that influences the amplitude or phase of an oscillating system.

For a single molecule, the decay is due to loss of energy

1) Interaction with environment (friction → heat or nonradiative relaxation)
2) Emission of radiation (radiative)

The decay rate is the given by the **lifetime**, T_1. ($\gamma = 1/T_1$) Linewidth: "lifetime broadening".

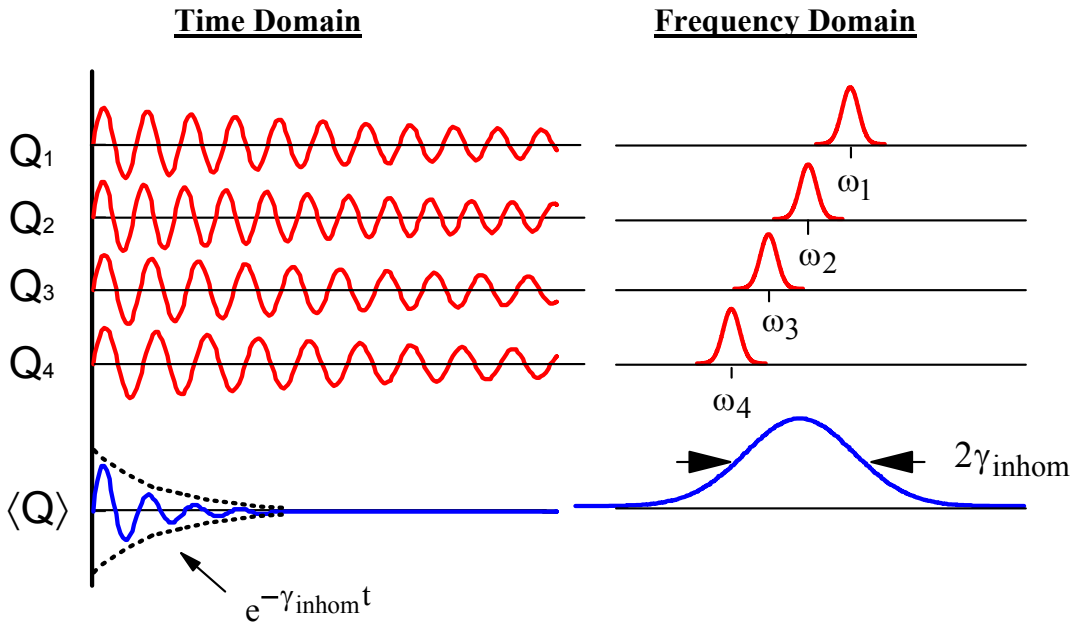
We make measurements on large numbers of molecules: "ensembles."

Properties of the collection can influence observed relaxation effects. For N molecules:

$$\langle Q(t)\rangle = \sum_{i=1}^{N} Q_i(t) = \sum_{i=1}^{N} A_i e^{-\gamma_i t}\sin(\Omega_i t)$$

For all molecules behaving *identically*: Observed decay rate is lifetime.

What happens if the frequencies are a bit different?



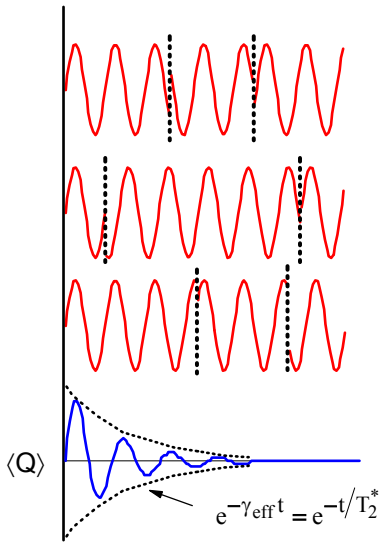
The microscopic damping is masked and the observed damping reflects the distribution in Ω_0.

What about phase?

We use a light field that drives all oscillators in phase, but the oscillator phase can vary in time → for instance, collisions.

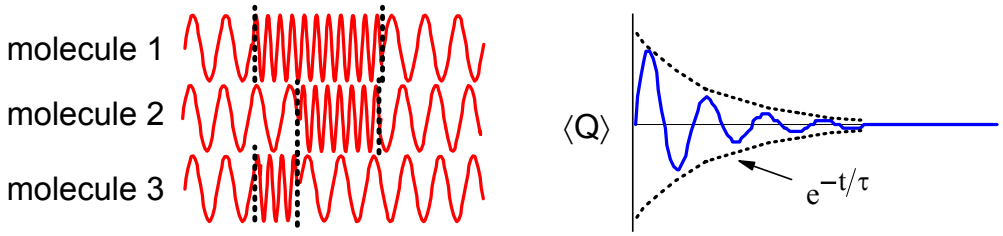
Destructive interference → **<u>pure dephasing</u>**

Pure dephasing time: T_2^*



There are other damping processes:

- For instance, in your NMR experiment you measure the rates of exchange between pyruvic acid and dihydroxypropanoic acid by measuring linewidths. This is dephasing due to exchange between two species with distinct frequencies:



When averaged over all molecules, the destructive interference due to hopping between sites leads to a decay that reflects the mean residence time, τ.

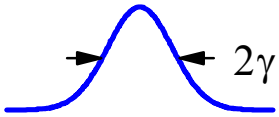
- Also, rotational motion also contributes to linewidth.

<u>All processes that influence the amplitude or phase of oscillations are observed in a spectrum.</u>

The damping rate of an ensemble is a sum over all relaxation rates:

$$\gamma = \gamma_{\text{lifetime}} + \gamma_{\text{dephasing}} + \gamma_{\text{inhom}} + \cdots$$

$$\frac{1}{T_2} = \frac{1}{T_1} + \frac{1}{T_2^*} + \cdots$$



How can you separate these in a spectrum? You can't *without additional measurement*.

in gas—organics mainly lifetime . . .
in room temperature solution—mainly dephasing (IR and electronic)
in low T systems (liquids/crystals) —γ_{inhom}