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**

\[
P_{\omega}(\omega) \quad 0 \omega \quad \gamma
\]

Vary frequency of driving field.
Disperse color → measure power absorbed

The variables \(\omega_0\) and \(\gamma\) characterize the time-dependent behavior of our H.O. So indeed we could measure these variables also if we applied a short driving force and watched the coordinate directly. It would oscillate and relax to equilibrium, and we would characterize \(\omega_0 + \gamma\) that way.

(2) **Watch coordinate** ↔ **Time domain**

\[
Q \quad 2\pi \quad \Omega_0
A e^{-\gamma t}
\]

short driving force → watch relaxation/oscillation

This is the basis for time-resolved spectroscopy using short pulses of light to exert an impulse response 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 Transformation:

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

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

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

**Time domain** \( S(t) \leftrightarrow Frequency domain \ S(\omega) \)

These are related through the Fourier Transform integrals:

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

( this gives \( S(t) \) if we know \( S(\omega) \) ) \quad ( 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:**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Time Domain ( S(t) )</th>
<th>Frequency Domain ( S(\omega) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large ( \omega_0 )</td>
<td>Fast oscillations</td>
<td>High frequency</td>
</tr>
<tr>
<td>Small ( \omega_0 )</td>
<td>Slow oscillations</td>
<td>Low frequency</td>
</tr>
<tr>
<td>Large ( \gamma )</td>
<td>Fast decay</td>
<td>Broad linewidth</td>
</tr>
<tr>
<td>Small ( \gamma )</td>
<td>Slow decay</td>
<td>Narrow linewidth</td>
</tr>
</tbody>
</table>
**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 – let’s call it seconds. The time period for oscillation \( 1/\nu = 10 \text{ sec} \) and the time scale for relaxation is \( 1/\gamma = 100 \text{ sec} \))

\[ S \] is the Fourier transform of \( C(t) \):

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 \( 2\gamma \). 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 \( (\nu_1 - \nu_2)/2 \).
2) Other examples:

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 \( \omega_1/2\pi = \nu_1 = 0.1; \ \omega_2/2\pi = \nu_2 = 0.125; \ \gamma_1 = 1/50; \ \gamma_2 = 1/10; \ A_1 = 3; \ A_2 = 5. \)

![Graph of superimposed oscillations](image1)

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

![Graph of sum of harmonics](image2)

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).

![Graph of rotational features](image3)

![Graph of rotational features](image4)
DAMPING

Damping is any process that influences the amplitude or phase of an oscillating system.

Let’s look more carefully at this:

For a single harmonic oscillator, the decay is due to loss of energy → friction

Molecule: 1) interaction with environment (heat – nonradiative)
2) emission of radiation (radiative)

This is known as lifetime broadening → $T_1$

We make measurements on large numbers of molecules: “ensembles.”

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

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

What happens if the frequencies are a bit different?

<table>
<thead>
<tr>
<th>Time Domain</th>
<th>Frequency Domain</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_1$</td>
<td>$\omega_1$</td>
</tr>
<tr>
<td>$Q_2$</td>
<td>$\omega_2$</td>
</tr>
<tr>
<td>$Q_3$</td>
<td>$\omega_3$</td>
</tr>
<tr>
<td>$Q_4$</td>
<td>$\omega_4$</td>
</tr>
</tbody>
</table>

$\langle Q \rangle$ 

$e^{-\gamma_{inhom} t}$

There are tricks for removing this: single-molecule spectroscopy / echo experiments
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 → pure dephasing

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:

  ![Diagram showing molecular exchange](image)

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

- Also, rotational motion is seen in linewidth.

All processes that influence the amplitude or phase of the oscillations are observed in a spectrum.
The damping rates of a collection of oscillators 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) —\( \gamma_{\text{inhom}} \)