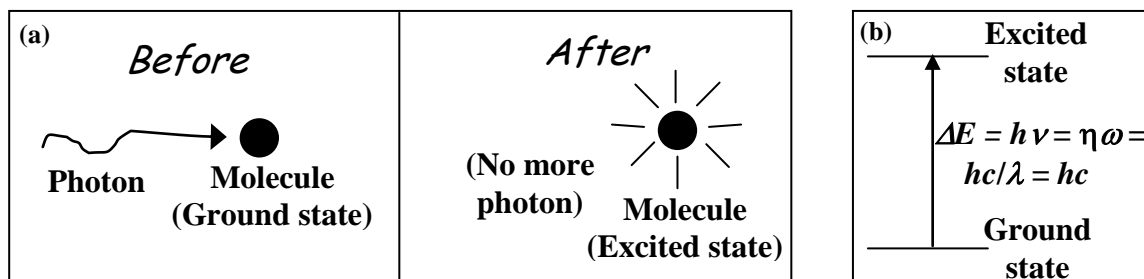


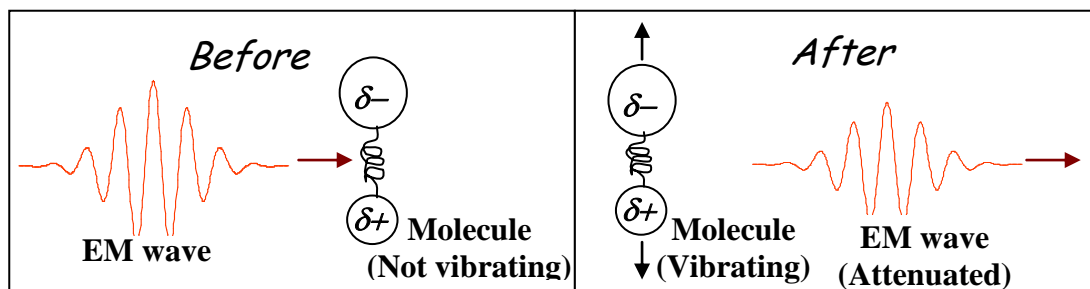
## Spectroscopy in frequency and time domains

Last time we introduced spectroscopy and spectroscopic measurement.

I. Emphasized that both quantum and classical views of spectroscopy are important



Quantum mechanical - light is photons (quanta of energy), molecule is discrete states with quantized energy levels



Classical mechanical - light is classical EM wave, molecule is classical oscillator with continuous vibrational amplitudes

In both cases, power absorbed is highest when the light frequency is *on resonance*.

The two pictures are compatible because *amplitude* is NOT equivalent to *energy* in QM. The system could be in a *stationary* state of high energy or it could be oscillating but an energy measurement has some probability of yielding zero excess vibrational energy.

II. We looked at the EM wave

$$\mathbf{E}(x, t) = \hat{\mathbf{e}} E_0 \cos(kx - \omega t + \phi)$$

Simpler form for molecules at fixed location ( $x = 0$ ) and neglecting polarization & phase

$$E(t) = E_0 \cos \omega t$$

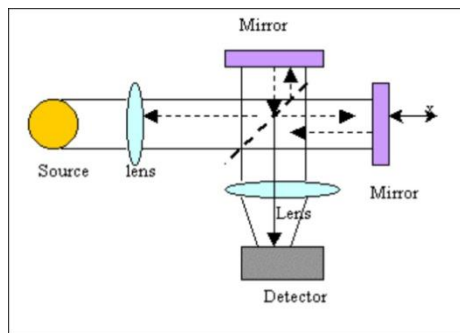
III. We looked at how a conventional spectrometer works and what it measures

Incident and transmitted light intensities at various frequencies are compared to determine the absorption spectrum of the sample

Image removed due to copyright restrictions. Please see:  
 Ocean Optics. [USB4000 Fiber Optic Spectrometer Installation and Operation Manual](#). Document Number 211-00000-000-02-201201. Appendix C, p. 27.

Beer's law:  $-\log(I/I_0) = \alpha(\omega) \cdot c \cdot L = A(\omega)$

IV. We looked at FTIR, our first example of Fourier transform spectroscopy



Interferometer measures the interference between two replicas of the field as one mirror is variably delayed, revealing the EM oscillation cycles in the "position" domain.

The frequency content of the field can be determined through Fourier transformation.

$$F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) \cos(\omega t) dt$$

$$f(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(\omega) \cos(\omega t) d\omega$$

or really FT between  $x$  and  $k$

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) \cos(kx) dx$$

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(k) \cos(kx) dk$$

Now we'll address how light interacts with the sample.

### The sample response to light

What happens to the sample when light hits it? How does light interact with matter?  
We'll consider IR light and molecular vibrations - similar for UV-VIS and NMR

Classical equation of motion

$$\mu \frac{d^2 Q(t)}{dt^2} + b \frac{dQ(t)}{dt} + KQ(t) = aE_0 \cos(\omega t)$$

$Q(t)$  is the time-dependent vibrational displacement

$\mu$  is the reduced mass

$b$  is a friction coefficient

$K$  is the force constant

$a$  is a coupling constant between the electric field of the light & the molecular vibration

Note: We will plug solutions for  $Q(t)$  into the equation of motion to see that they work, but you will not need to find solutions for  $Q(t)$  on your own.

*You do not need math beyond basic calculus for any aspect of this module*

Simplest case: No driving force, no damping

Solution:  $Q(t) = Q_0 \cos(\omega_0 t)$  with *resonance frequency*  $\omega_0 = \sqrt{K/\mu}$ .

With damping:  $Q(t) = Q_0 e^{-\gamma t} \cos(\Omega t)$

$\gamma = b/2\mu$  is the *damping constant*

oscillation frequency  $\Omega = \sqrt{\omega_0^2 - \gamma^2}$

With the driving force:

Solution:  $Q(t) = A \sin(\omega t + \beta)$

$$A(\omega) = \frac{aE_0/\mu}{\left[ (\omega^2 - \omega_0^2)^2 + 4\gamma^2 \omega^2 \right]^{1/2}}$$

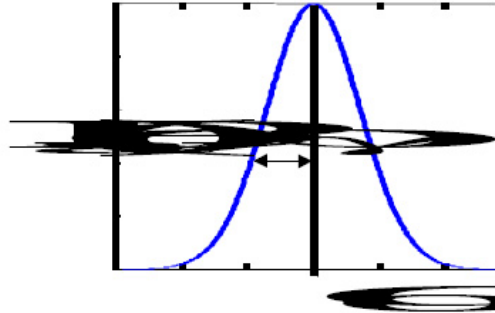
Vibrational amplitude  $A(\omega)$  increases as the driving frequency approaches the resonance frequency  $\omega_0$ . The vibrational amplitude depends linearly on the driving field amplitude.

The vibrational oscillations are in phase with the driving force ( $\beta = \pi/2$ ) when driven far off resonance, out of phase ( $\beta = 0$ ) when driven on resonance.

Power absorbed: *force x velocity*. Averaged over one or many cycles:

$$P(\omega) = \frac{(aE_0)^2}{\mu} \frac{\gamma\omega^2}{(\omega^2 - \omega_0^2)^2 + 4\gamma^2\omega^2} \approx \frac{(aE_0)^2}{4\mu} \frac{\gamma}{(\omega - \omega_0)^2 + \gamma^2} \quad (5)$$

*Lorentzian* function for the absorption spectrum, with width given by the damping constant  $\gamma$ .



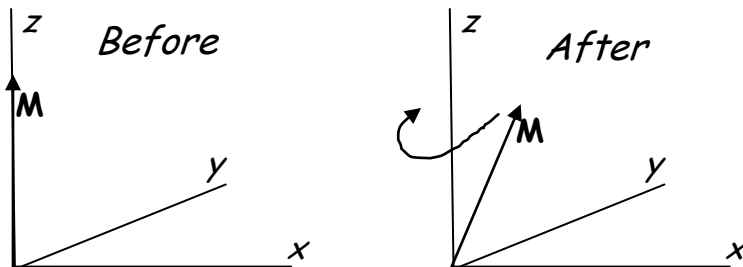
This is what is measured in an absorption spectrum: how much power gets absorbed from the incident light at each frequency

Note that  $\gamma$  is really a dephasing rate, which may be due to ordinary damping (loss of vibrational energy) but may be loss of vibrational phase coherence even when energy is retained. More on this later.

### Measurements in the time domain

NMR: measure  $Q(t) = Q_0 e^{-\gamma t} \cos(\Omega t)$  directly

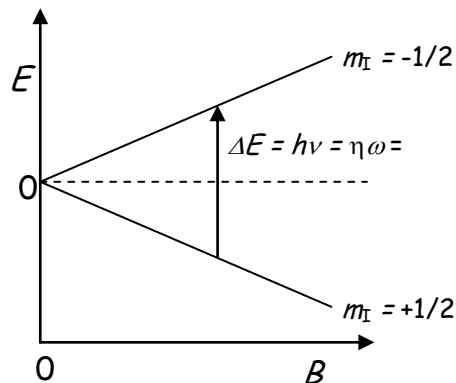
RF pulse induces net magnetization vector  $\mathbf{M}$  to precess about  $z$  axis (permanent applied magnetic field direction). The component of  $\mathbf{M}$  along  $x$  or  $y$  undergoes damped oscillations.



Vibrational & electronic oscillations also can be measured on ultrafast (femtosecond) time scales.

In NMR, the frequency depends on the applied magnetic field in the z direction. The magnetic field strength dictates how big is the restoring force for spins to align in that direction.

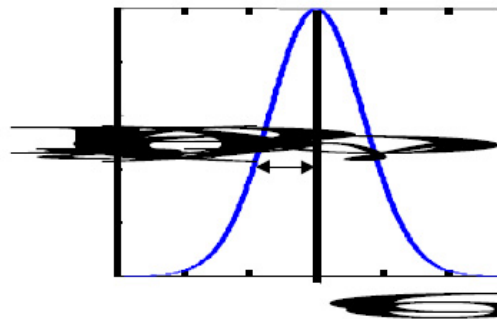
QM picture: two spin energy levels given by z-component magnetic moment quantum number  $m_I = \pm \frac{1}{2}$ :



Proton spin energy levels as a function of applied magnetic field  $B$ . The proportionality constant  $\gamma_p$  (no relation to any damping rate) is called the gyromagnetic ratio.

$Q(t) = Q_0 e^{-\gamma t} \cos(\Omega t)$  gives Lorentzian absorption spectrum through FT.

$$A(\omega) \propto \frac{\gamma}{(\omega - \omega_0)^2 + \gamma^2}$$



Compare generally the time domain and frequency domain signals:

<u>Parameter</u>	<u>Time Domain <math>S(t)</math></u>	<u>Frequency Domain <math>S(\omega)</math></u>
Large $\omega_0$	Fast oscillations	High frequency
Small $\omega_0$	Slow oscillations	Low frequency
Large $\gamma$	Fast decay	Broad linewidth
Small $\gamma$	Slow decay	Narrow linewidth

FT relation applies to any type of spectroscopy and to any time or frequency dependence!  
Reproduces multiple peaks, complex lineshapes, etc.

*Dephasing rate*  $\gamma$  has several contributions:

**Damping** - the energy decays back to zero

This happens because the vibrating molecule interacts ("collides") with other molecules and gradually stops vibrating. The vibrational energy goes into other degrees of freedom - other vibrational modes of the same molecule or of other molecules, or molecular rotational or translational motion

**"Pure" dephasing** - the energy stays the same but the coherence decays away

This happens because the vibrating molecule interacts ("collides") with other molecules and the vibrational phase gets shifted

**Inhomogeneous dephasing** - the energy stays the same, and the coherence remains for any individual molecule, but the collective coherence decays

This happens because different molecules might have slightly different vibrational frequencies due to somewhat different environments. After awhile the oscillations at different frequencies go out of phase

All these effects lead to decay of net (superposed) oscillation amplitude in the time domain and to broadening of the absorption line in the frequency domain

The time and frequency domain signals are always related through Fourier transformation, regardless of the cause of dephasing

All these dephasing contributions can occur with magnetic spins, molecular vibrations, and electronic transitions

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