5.33 Lecture Notes: Introduction to Spectroscopy

What is spectroscopy?

Studying the properties of matter through its interaction with different frequency components of the electromagnetic spectrum.

Latin: "spectron"—ghost or spirit
Greek: "σκοπειν"—to see

With light, you aren't looking directly at the molecule—the matter—but its "ghost." You observe the light's interaction with different degrees of freedom of the molecule. Each type of spectroscopy—different light frequency—gives a different picture → ***the spectrum***.

Spectroscopy is a general methodology that can be adapted in many ways to extract the information you need (energies of electronic, vibrational, rotational states, structure and symmetry of molecules, dynamic information).

Goals:

- Understand how light interacts with matter and how you can use this to *quantitatively* understand your sample.
- Understand spectroscopy the way you understand other common tools of measurement like the watch or the ruler.
- See that *spectroscopy is a set of tools that you can put together in different ways to understand systems* → solve chemical problems.

The immediate questions that we want to address are:

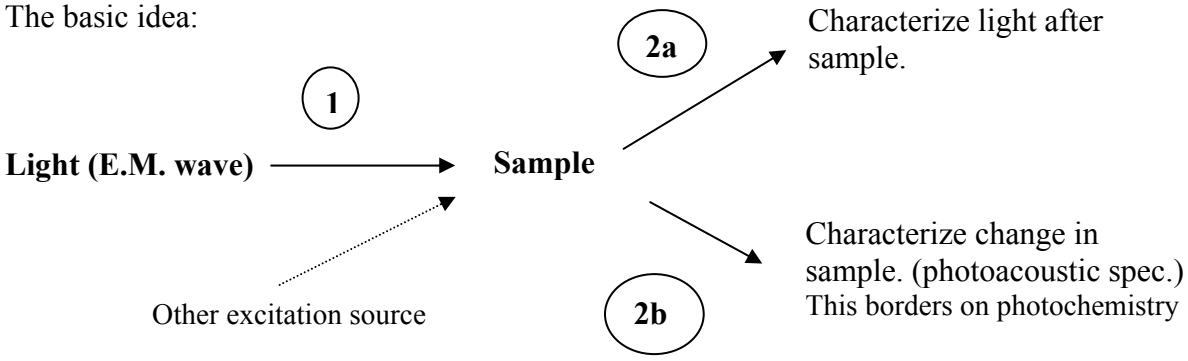
- What does light do to sample?
- How do you produce a spectrum?
- What EXACTLY is a spectrum a measurement of?

What does a spectrum measure?

Interaction of light with a sample can influence the sample and/or the light.

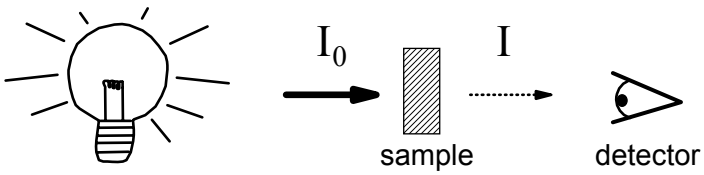
Method involves: (1) excitation and (2) detection.

The basic idea:

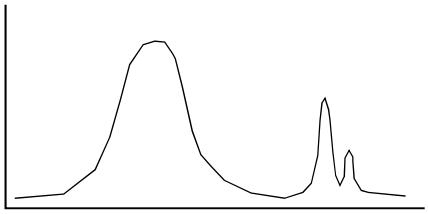


In most spectroscopies, we characterize how a sample modifies light entering it.

1) **<u>Absorption:</u>** Change in intensity **I** of incident light
Sample attenuates light → transmission $\mathbf{T=I/I_0}$



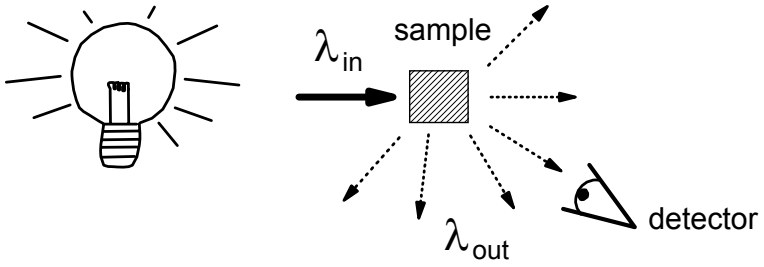
We measure the absorption of light at different frequency or wavelength.



ω/λ/ν (characteristic frequency/wavelength of light entering sample)

2) **<u>Emission:</u>** Excitation induces emission of light from the sample (usually of different frequency).

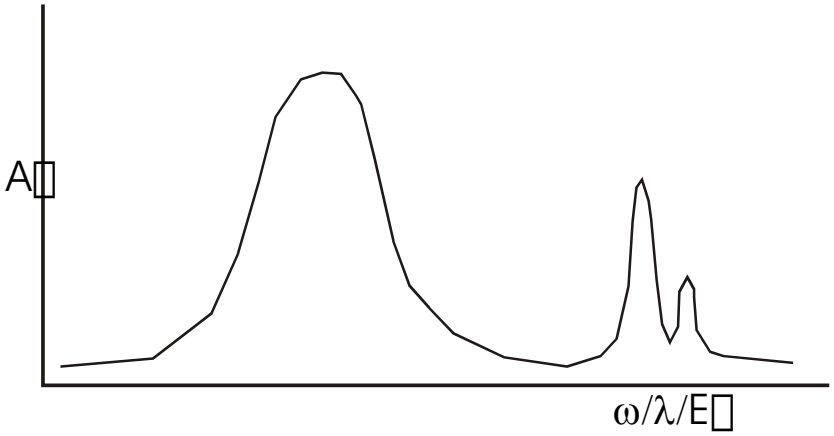
(Emitted in all directions)



Includes: **Fluorescence** (emission from excited electronic singlet states)
Phosphorescence (emission from excited electronic triplet states)
Raman Scattering (light scattering involving vibrational transition)

3) **<u>Optical Rotation:</u>** Change of phase of light incident on sample (rotation of polarization)

Let's work on describing absorption.



Let's look at a typical absorption spectrum.

What are the axes?

X-axis: Characterizes the input light in terms of frequency-wavelength-energy

Wavelength λ (nm, μm, Å),

Frequency ν (cycles/sec or s^{-1} or Hz) $= \frac{\omega}{2\pi} = \frac{c}{\lambda}$

$\omega = 2\pi\nu$ (rad/sec) (angular frequency)

$\bar{\nu} = \omega/2\pi c = 1/\lambda$ expressed in units of cm^{-1} (wavenumbers)

Energy $E = h\nu$ (expressed as eV or as cm^{-1} using $E/hc = \nu/c$)

Conversions

$\bar{\nu}\ (cm^{-1}) = 10^7 / \lambda(nm)$

$\bar{\nu}\ (eV) = 1240 / \lambda(nm)$

y-axis:

Absorption

$$A(\nu) = -\log\frac{I}{I_0} = \varepsilon(\nu)\, c\, L \qquad \text{(Beer's Law)}$$

I_0 = light intensity incident on the sample
I = light intensity after the sample
ε = molar decadic extinction coefficient $\left(M^{-1}cm^{-1}\right)$ – the molecular quantity
c = concentration (M)
L = sample length (cm)

This comes from assuming that the fraction of light absorbed as you propagate though the sample is proportional to the distance traversed: $dI/I = -\alpha\, dx$

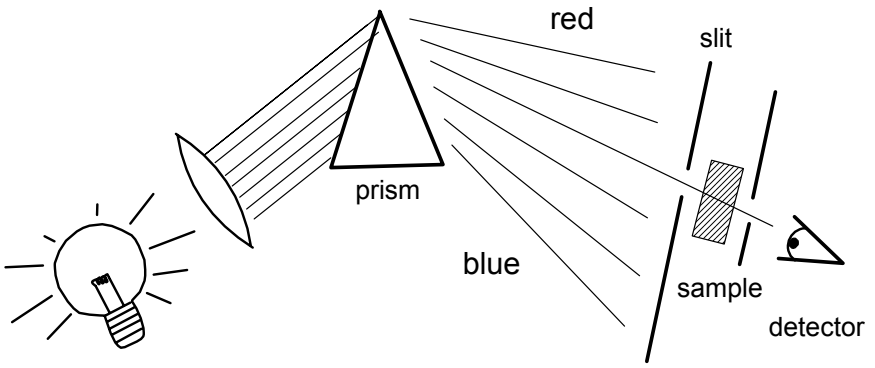
How do your measure absorption spectra?

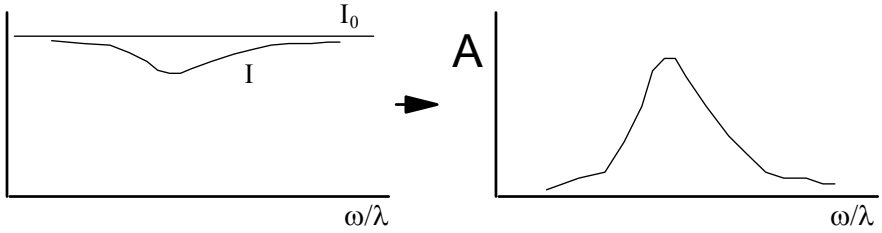
Measure the change of intensity of light at different frequencies as it passes through a sample.

Two types of spectrometers:

1) Dispersive
2) Fourier transform

Dispersive spectrometer: Separate different frequency components





Well talk about Fourier transform spectrometers later.

This is a way of processing all wavelength/frequencies simultaneously → IR/NMR