

SPECTROSCOPY

5.35 Module #1

Introduction to spectroscopy

Spectroscopy permits measurement of a tremendous amount of information, often in a very simple way.

Module consists of UV-VIS, fluorescence, IR, and NMR spectroscopy experiments

You'll use spectroscopy to probe:

Electronic orbitals of molecules & quantum dots (UV-VIS, fluorescence)

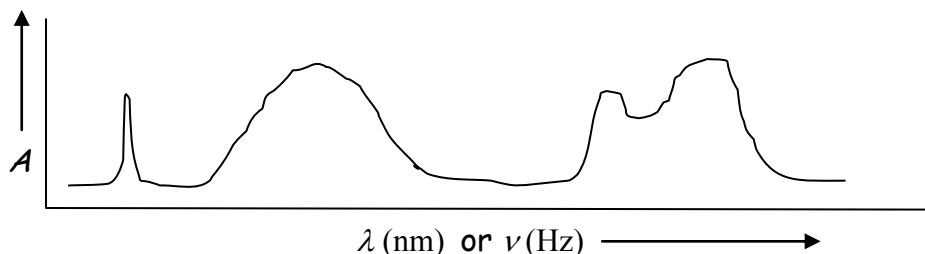
Vibrations of molecules (IR)

Spin states of protons in small molecules & proteins (NMR)

And you'll learn how spectroscopy works! Seek an understanding that permits creative use of spectroscopy to measure the information that you need, in whatever way allows it to be determined.

Light absorption

Absorption spectra reveal the frequencies at which light absorption occurs. These reveal molecular resonances and energy levels, structure and dynamics.



The y-axis is absorptivity

The x-axis is frequency or wavelength, measured in units that are reasonable for the part of the spectrum you're in.

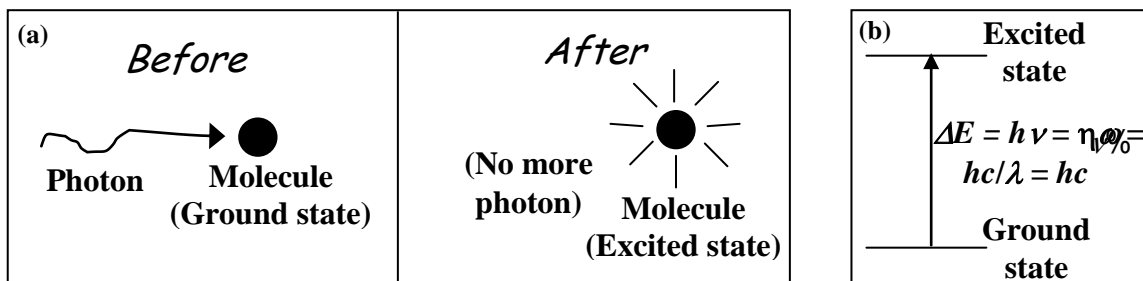
Why is light absorbed at some frequencies and not others?

5.111 & 5.112 picture of light absorption: purely **quantum mechanical**

Light represented as photons, molecule represented as quantized energy levels

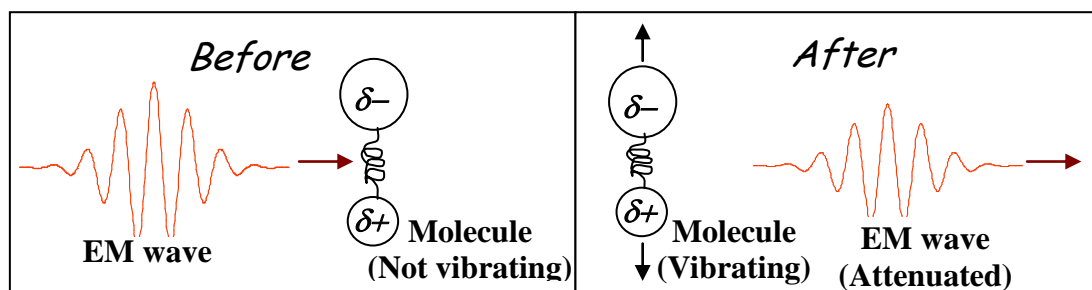
Correctly conveys conservation of energy

Photon energy = difference between quantum state energies



Important information is not conveyed in this picture. Molecule does not generally end up in a stationary state!

Classical mechanics: complementary picture of light absorption.



Light represented as a classical electromagnetic wave.

Molecule represented as a classical harmonic oscillator, driven by the EM field

Both pictures convey important information!

We'll rely on the classical picture mostly, since your physical intuition is classical.

To understand spectroscopy, it's essential to understand three things.

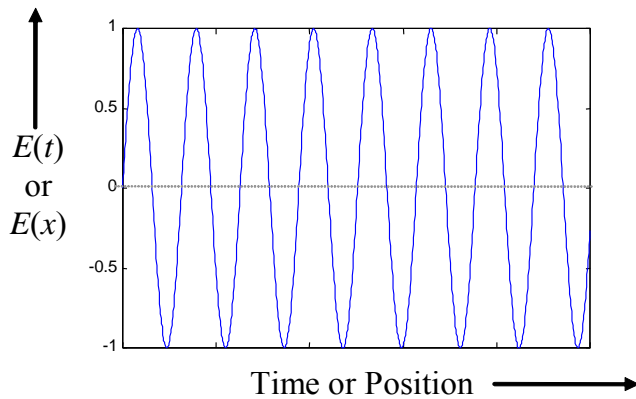
What is light?

What is matter?

How do they interact?

The electromagnetic (EM) field: What it is and how it can be measured

We'll examine the electric field first, the magnetic field later for NMR



For a single frequency:

$$\mathbf{E}(x,t) = \hat{\mathbf{e}} E_0 \cos(kx - \omega t + \phi) \quad (1)$$

Note the various features;

Polarization unit vector $\hat{\mathbf{e}}$ (assumed time-independent)

Amplitude E_0 (assumed time-independent)

Oscillating part. A propagating wave oscillates in *time and space*.

Temporal oscillation period $T = 2\pi/\omega$. **Frequency** ω in units of rad/s or s^{-1} .

Alternate frequency variable $\nu = 1/T = 2\pi\omega$, units cycles/sec or Hz.

Spatial oscillation period = *wavelength* = $\lambda = 2\pi/k$.

$k \equiv$ **wavevector**, in units of m^{-1} .

Sometimes we use "wave number" variable $\nu = 1/\lambda$, in units of cycles/m or cm^{-1}

Phase ϕ (assumed time-independent)

Light speed in vacuum $c = 3 \times 10^8$ m/s = $\lambda/T = \lambda\nu = \omega/k$.

Simplified scalar expression for the field at one position:
(neglecting polarization & phase)

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

Please see: [The Electromagnetic Spectrum](#)

Absorption spectroscopy

To record an absorption spectrum, we need lots of frequency components.

$$E(t) = E_1 \cos \omega_1 t + E_2 \cos \omega_2 t + E_3 \cos \omega_3 t + \dots = \int d\omega E_0(\omega) \cos \omega t$$

(Note we've neglected polarization & phase)

Usually the distribution of frequencies $E_0(\omega)$ is smoothly varying. How to measure it, before and after a sample?

Absorption spectrometer

UV-VIS spectrometer schematic illustration

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.

Ocean Optics UV/VIS Spectrometer (from instruction manual). 1 optical fiber connection, 2 slit, 3 filter, 4 collimating mirror, 5 grating, 6 focusing mirror, 7 collector lens, 8 detector.

Diffraction grating separates the frequency components

Intensity of each is measured at a CCD

Intensity $I = \frac{c}{4\pi} |E_0|^2$ (units of Watt/m² = Joule/s/m²)

Change in light intensity $dI(\omega)$ at any frequency due to sample absorption: Proportional to - incident intensity $I_0(\omega)$

- concentration c of the absorbing species
- absorptivity $\alpha(\omega)$ of the sample, discussed much further later
- for an infinitesimal sample, the thickness dL

$dI(\omega) = -\alpha(\omega) c dL I_0(\omega) \approx -\alpha(\omega) c dL I(\omega)$ where $I(\omega)$ is intensity after the sample

$dI(\omega)/I(\omega) = -\alpha(\omega) c dL$ can be integrated to derive Beer's Law (do the derivation!)

Result for macroscopic (thick) sample: $-\log(I/I_0) = \alpha(\omega) \cdot c \cdot L = A(\omega)$

$A(\omega)$ is typically displayed in an absorption spectrometer. If concentration c is in units of molecules/cm³, then $\alpha(\omega)$ is in units of cm². If concentration is in moles/liter, then $\alpha(\omega)$ is usually written as $\epsilon(\omega)$, the extinction coefficient, in units of liter/mole-cm.

We'll treat $\alpha(\omega)$ or $A(\omega)$ below by deriving the power absorbed by a classical oscillator when it's driven by a periodic force of frequency ω .

Fourier transform spectroscopy (FTIR)

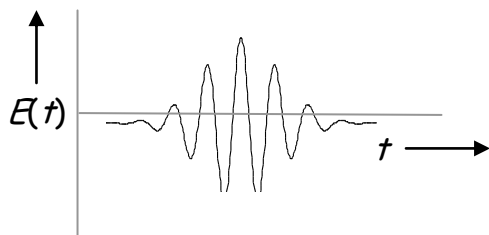
Instead of separating frequency components, could measure the time-dependent field

Simple example: *Gaussian* distribution of frequencies, peaked at ω_p with bandwidth δ .

$$E(t) = \int_{-\infty}^{\infty} d\omega E_0 e^{-[(\omega-\omega_p)/\delta]^2} \cos \omega t \propto e^{-(t/\tau)^2} \cos(\omega_p t)$$

with $\delta = 1/(2\tau)$.

Light field *temporal profile* is a *pulse* with a *Gaussian* time dependence and a duration, τ , that is given by the inverse of the spectral bandwidth. Let's look at such a pulse.



Pulse is short because many frequency components go out of phase and cancel at long times. **Broader frequency range \leftrightarrow shorter pulse duration**

Integral above is a *Fourier integral*. In general, $f(t)$ and $F(\omega)$ are *Fourier transforms* of each other if they are related through the following integrals.

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

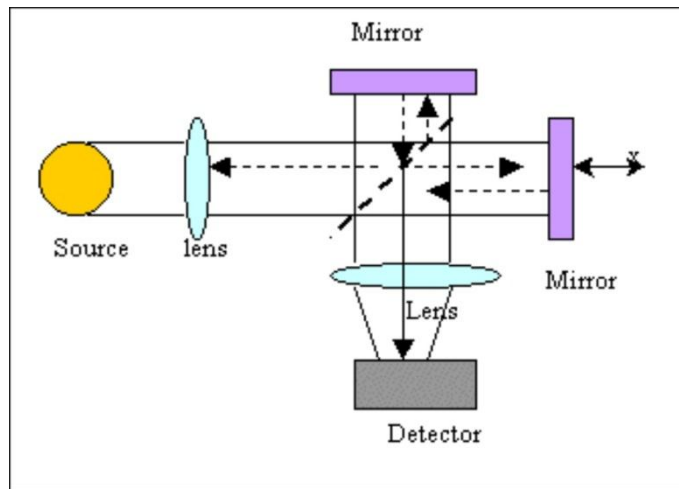
$$f(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(\omega) \cos(\omega t) d\omega$$

General result: We can measure the time-dependence of the field - whatever it is, Gaussian or otherwise - and determine the frequency-dependence taking the inverse Fourier transform as shown above.

The field can be fully characterized through measurement, and mathematical description, in the *frequency domain* (measure the amplitude of each frequency component, and if needed the phase also) or in the *time domain* (measure the time-dependent profile of the field).

How can we determine the time-dependent profile of a light field? It oscillates too fast to measure electronically.

Can measure the field *optically* with an *interferometer*.



Beamsplitter (dashed line) transmits and reflects equal parts of the light which return to the beamsplitter after reflection off the mirrors. Depending on mirror positions, they interfere constructively or destructively. Detector measures oscillating intensity as function of mirror position!

$$I(t') = I_0 [1 + \cos \omega t']$$

where t' is the temporal delay between the two fields. In terms of the spatial delay x'

$$I(x') = I_0 [1 + \cos kx']$$

"Position" domain measurement of the field

Fourier transform of

$$I(k) = \int_{-\infty}^{\infty} dx' I(x') \cos kx'$$

gives output as a function of wavelength through relation $\lambda = 2\pi/k$

or as a function of frequency through relation $\omega/k = c$

As before, make measurement with & without sample in place, and compare results to determine absorption spectrum.

Works the same way in FTIR even with an incoherent (or partially coherent) light source

The sample response to light

Classical equation of motion

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

Q is the vibrational coordinate

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: Like the classical equations of motion generally, this is a *differential equation*

Techniques for solving differential equations are taught in a math course on differential equations!

We are going to look at solutions of this equation, and you should plug them in to verify that they solve it, but you are never going to have to solve a differential equation on your own in this module!!

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

Simplest case: No driving force, no damping

Initial condition: Stretch the spring to some initial displacement Q_0 , and let go

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

Next simplest case: No driving force, but damping included

Initial condition: Stretch the spring to some initial displacement Q_0 , and let go

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

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

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

Full treatment: Driving force included, damping included

Assume steady state - driving force is on forever

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

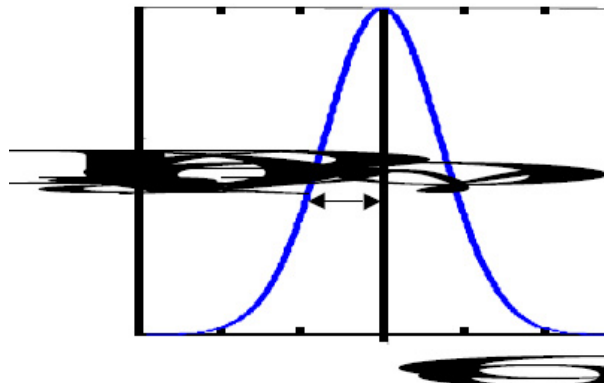
$$A(\omega) = \frac{aE_0/\mu}{\left[(\omega^2 - \omega_0^2)^2 + 4\gamma^2 \omega^2 \right]^{1/2}}$$

Vibrational amplitude $A(\omega)$ increases as the driving frequency approaches the resonance frequency ω_0 . The vibrational amplitude depends linearly on the driving field amplitude.

Power absorbed: *force x velocity*. We're interested in the power averaged over a cycle of the light.

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

Lorentzian function for the absorption spectrum, with width given by the damping constant γ .



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