Spectroscopy and Applications

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).

I want you to understand how light interacts with matter and how you can use this to *quantitatively* understand your sample.

I want you to understand spectroscopy the way you understand other common tools of common measurement like the watch or the ruler.

You will 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:

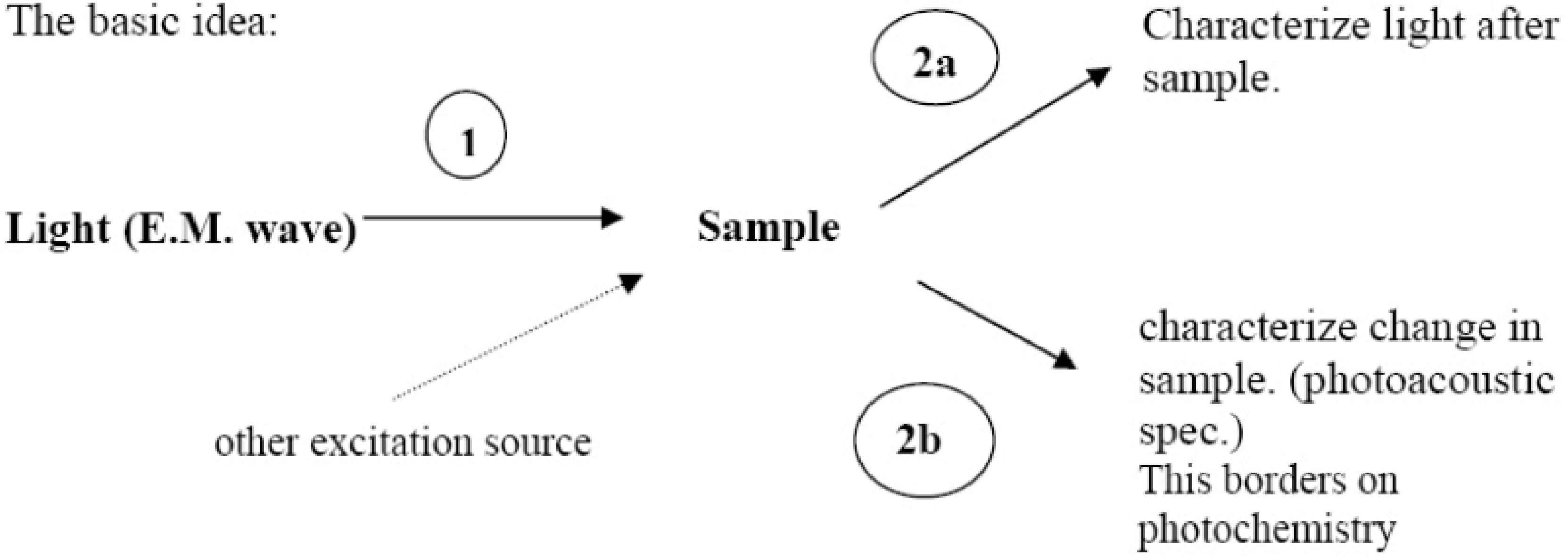
- What does light do to sample?
- How do you produce a spectrum?
- What EXACTLY is a spectrum a measurement of?

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:



Light (E.M. wave)

①

other excitation source

Sample

2a

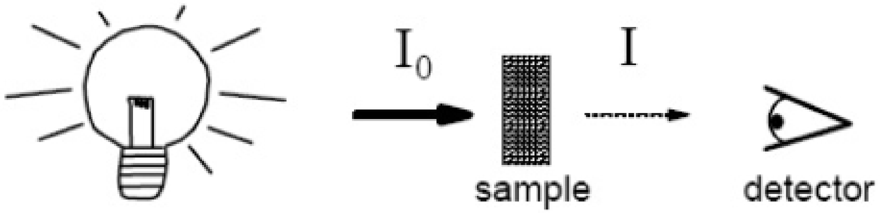
Characterize light after sample.

2b

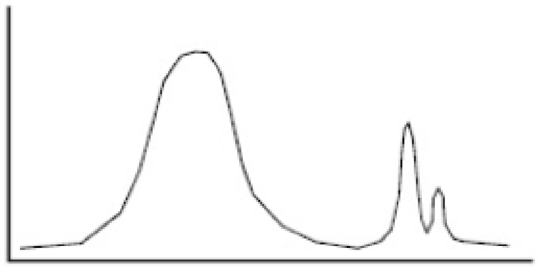
characterize change in sample. (photoacoustic spec.)
This borders on photochemistry

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

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

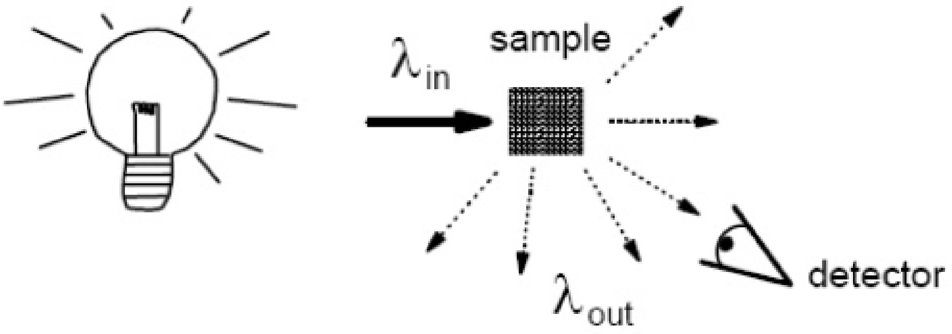


We measure the absorption of light at different frequency/wavelength



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

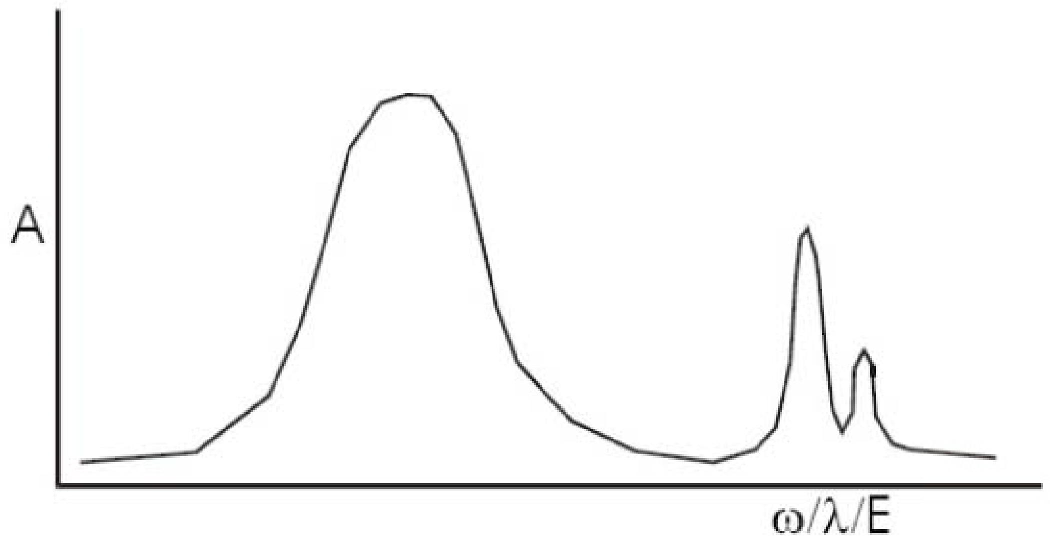
2) **Emission:** **(or scattering)** Excitation induces emission of light from the sample (usually of different frequency).



(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) **Optical Rotation:** Change of phase of light incident on sample (rotation of polarization)



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) $= \dfrac{\omega}{2\pi} = \dfrac{c}{\lambda}$

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

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

Energy $E = h\nu$ (usually expressed 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 that got through the sample
ε = molar decadic extinction coefficient $\left(M^{-1}cm^{-1}\right)$ – the molecular quantity
c = concentration (M)
L = sample length (cm)

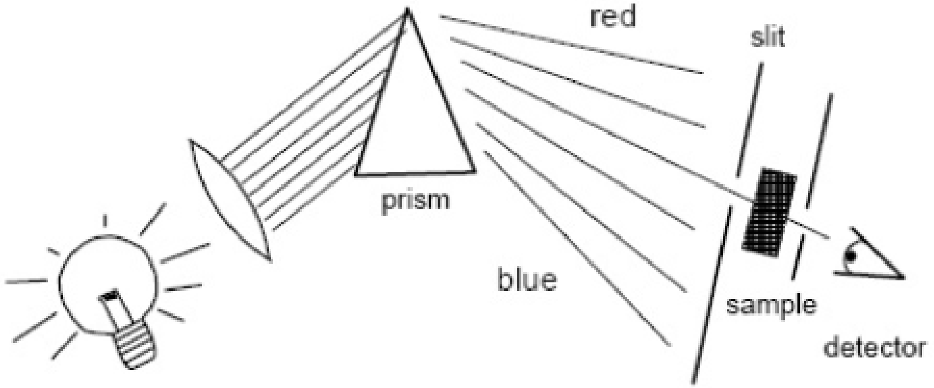
How do your measure absorption spectra?

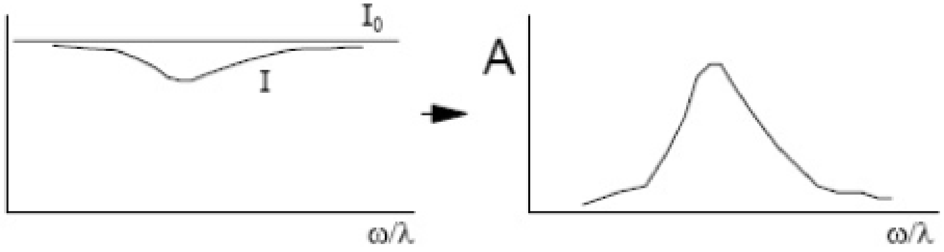
Measure the change of intensity of light at different frequencies as it passes through a sample.

Two types of spectrometers:

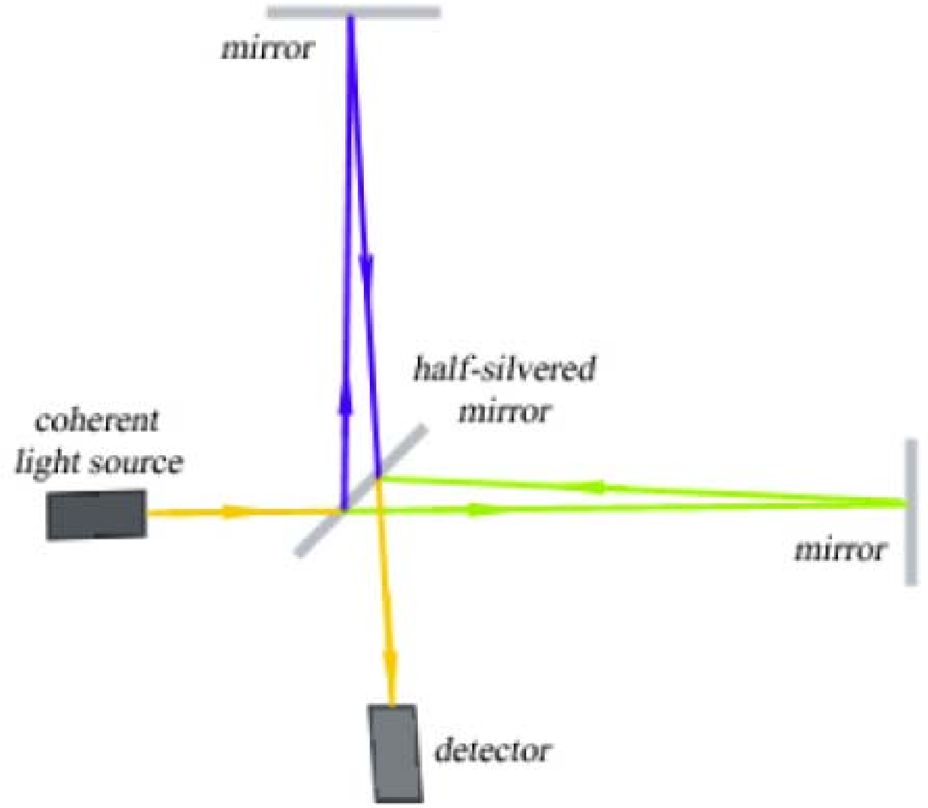
1) Dispersive
2) Fourier transform

Dispersive spectrometer: Separate different frequency components

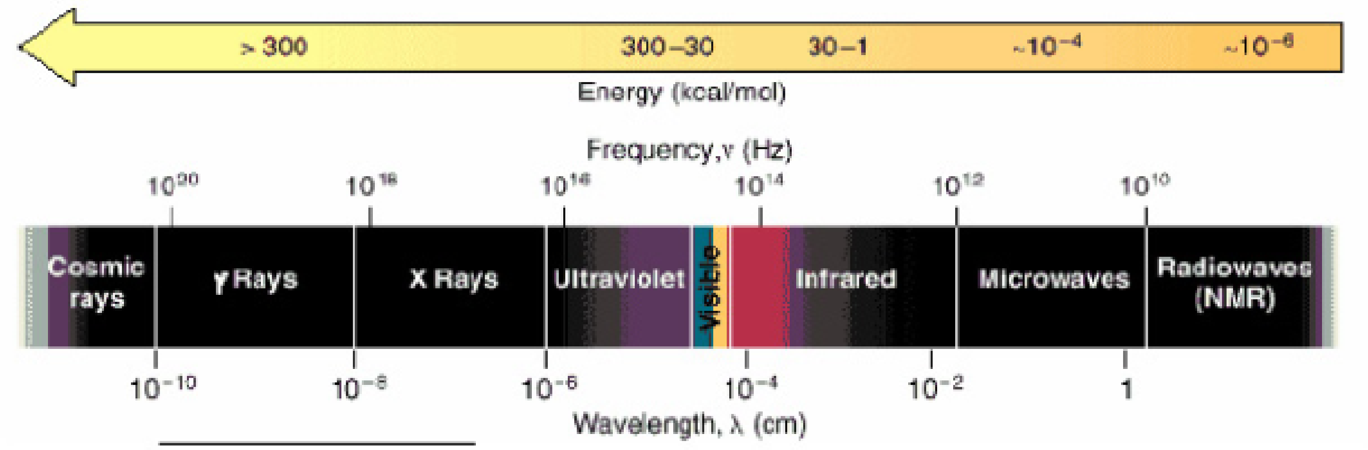




Fourier Transform Spectrometer



Introduction to Spectroscopy: The Electromagnetic Spectrum



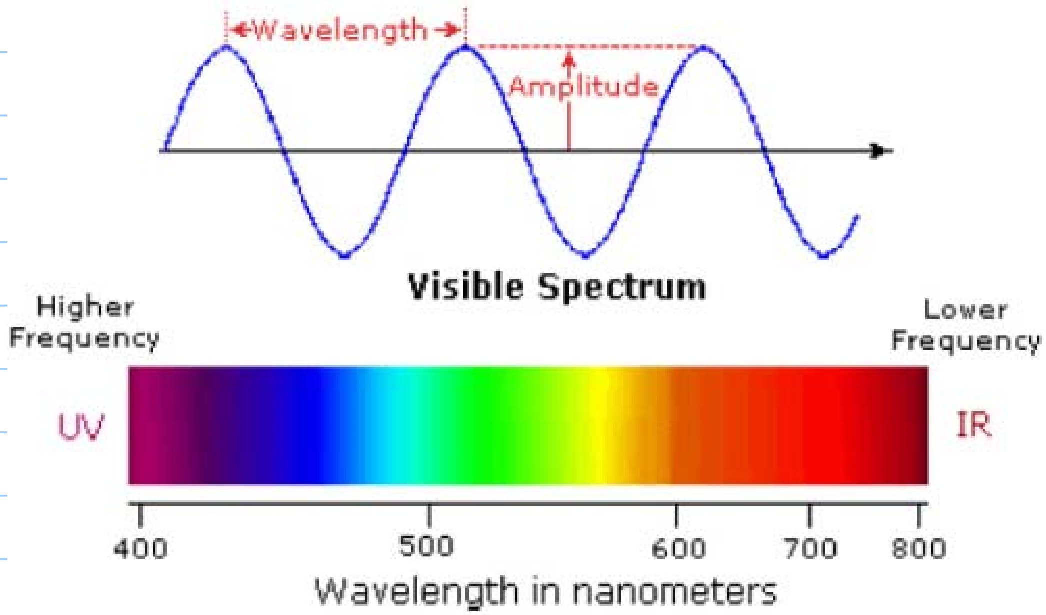
•**<u>UV-Vis</u>:** Excitation of electronic energy states, e.g. $\pi-\pi^*$ transition (30-140 Kcal/mol difference between electronic states).

•**<u>IR</u>:** Excitation of vibrational energy states, i.e. stretching and bending of chemical bonds. Organic functional groups have characteristic IR absorptions (1-10 Kcal/mol difference between vibrational states).

•**<u>Microwaves</u>:** Excitation of rotational energy states (1 Kcal/mol difference between rotational states).

•**<u>Radio waves</u>:** Excitation of nuclear spin states (0.0000286 Kcal/mol difference between rotational states).

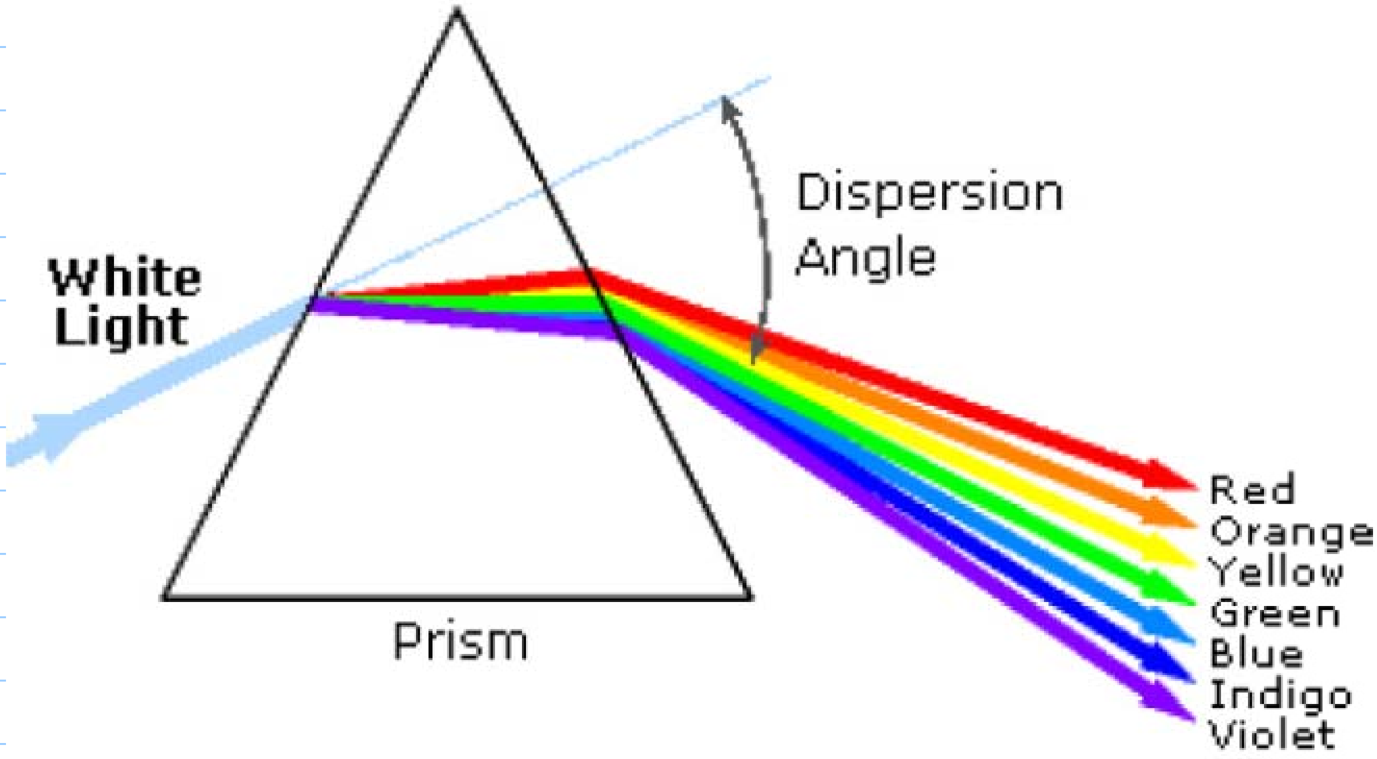
Visible Spectrum



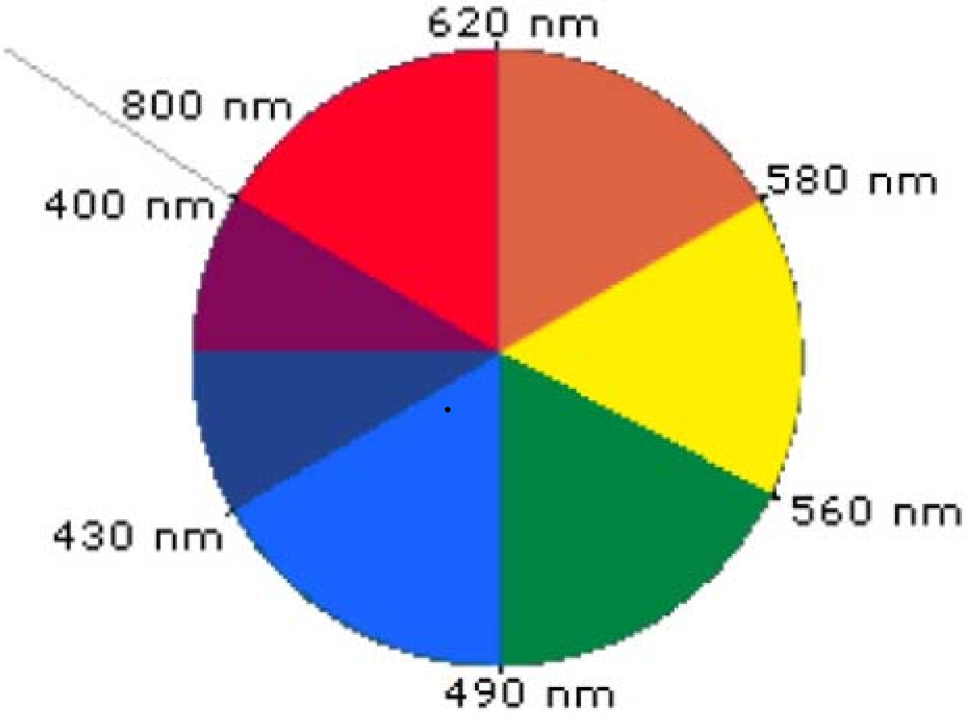
- **Violet:** 400 - 420 nm
- **Indigo:** 420 - 440 nm
- **Blue:** 440 - 490 nm
- **Green:** 490 - 570 nm
- **Yellow:** 570 - 585 nm
- **Orange:** 585 - 620 nm

- **Red:** 620 - 780 nm

Dispersion

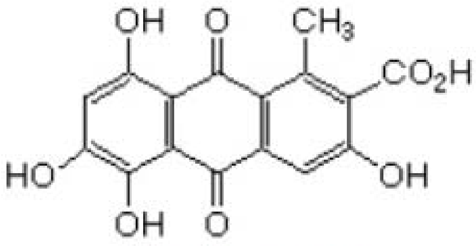

White Light
Prism
Dispersion Angle
Red
Orange
Yellow
Green
Blue
Indigo
Violet

Color Wheel Eye as a Spectrometer

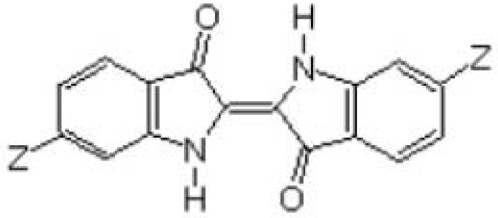


complimentary colors

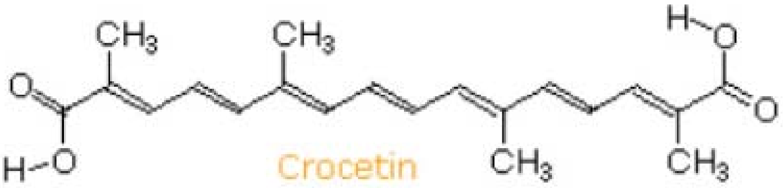
Some Natural Organic Pigments



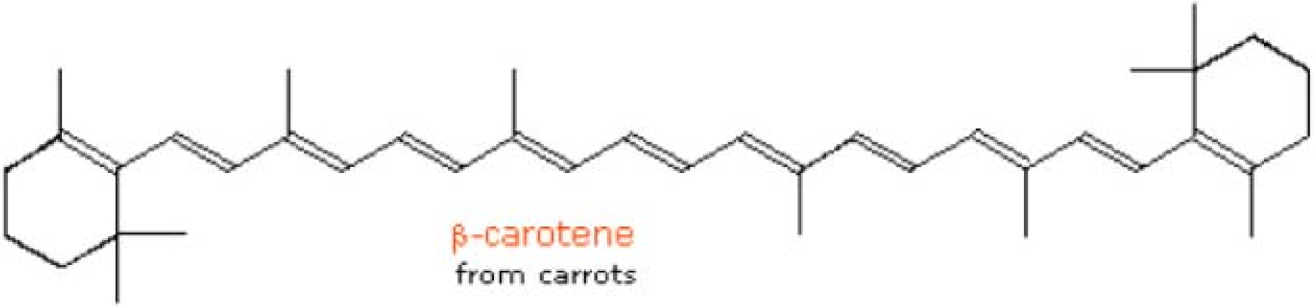
Kermesic Acid
(Carminic Acid)
from the insect *Coccus cacti*



Z=H
Indigo
from *Isatis tinctoria* (woad)
Z=Br
Punicin or Tyrian Purple
from mollusks of the genus *Murex*

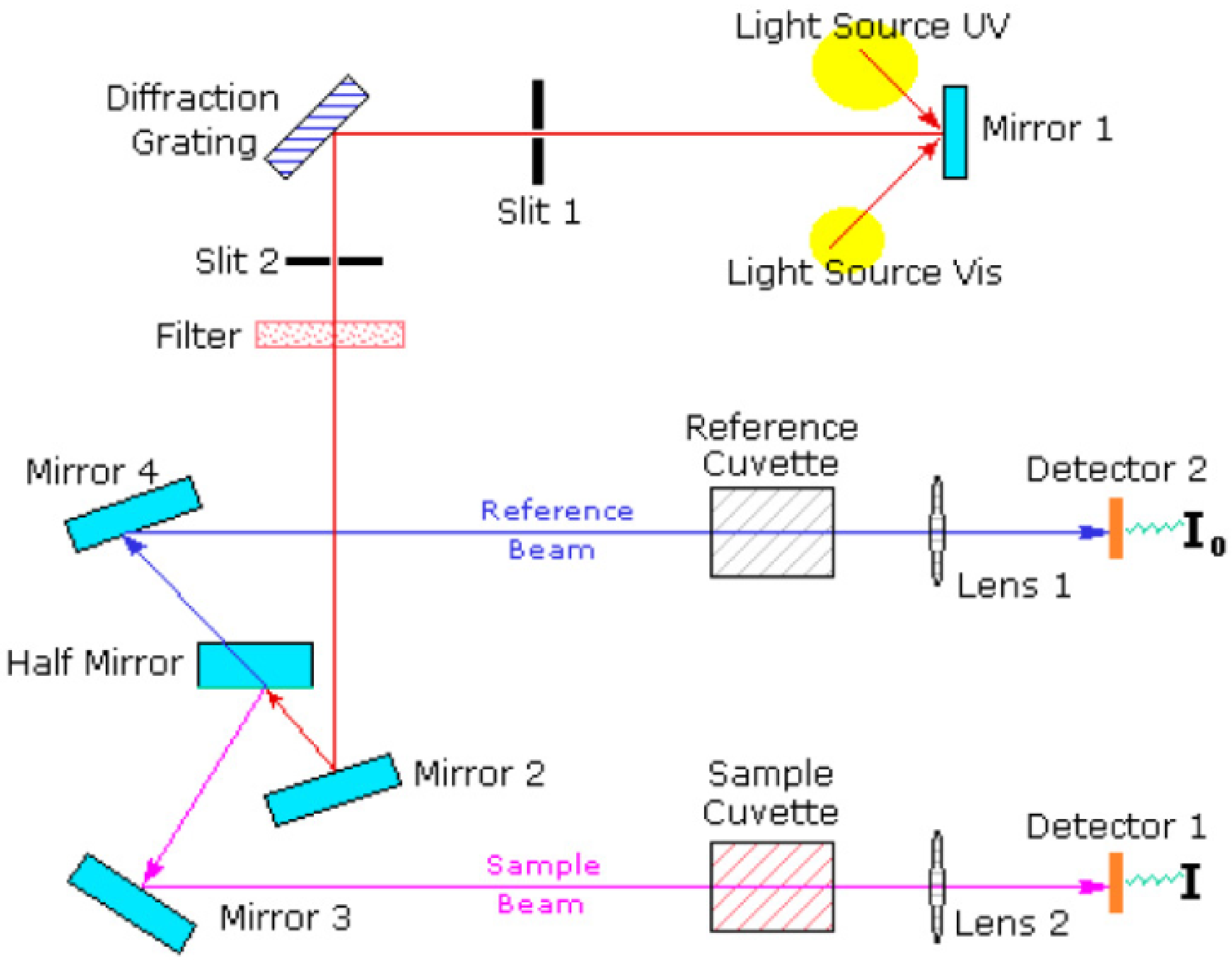


Crocetin
from saffron

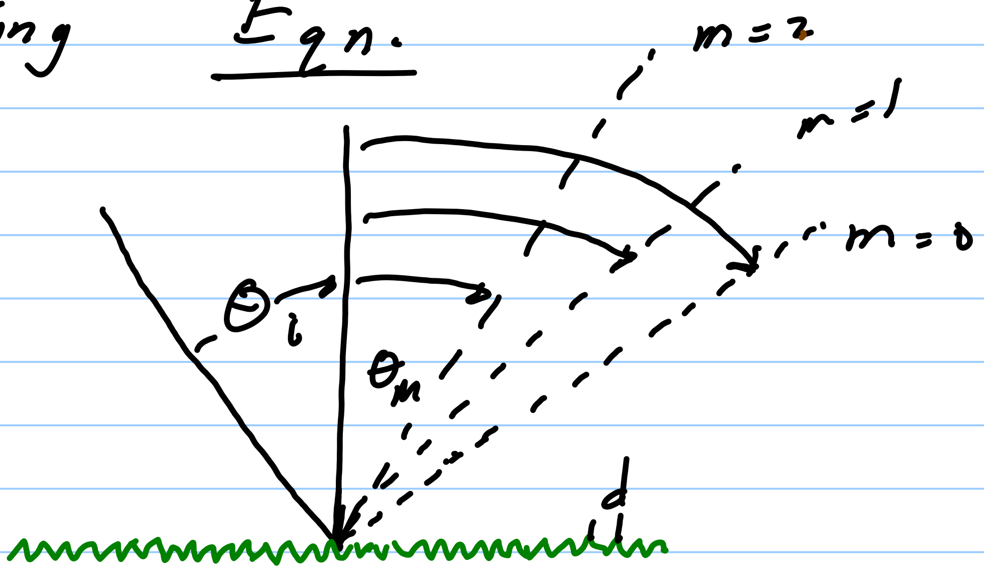


β-carotene
from carrots

Spectrometer



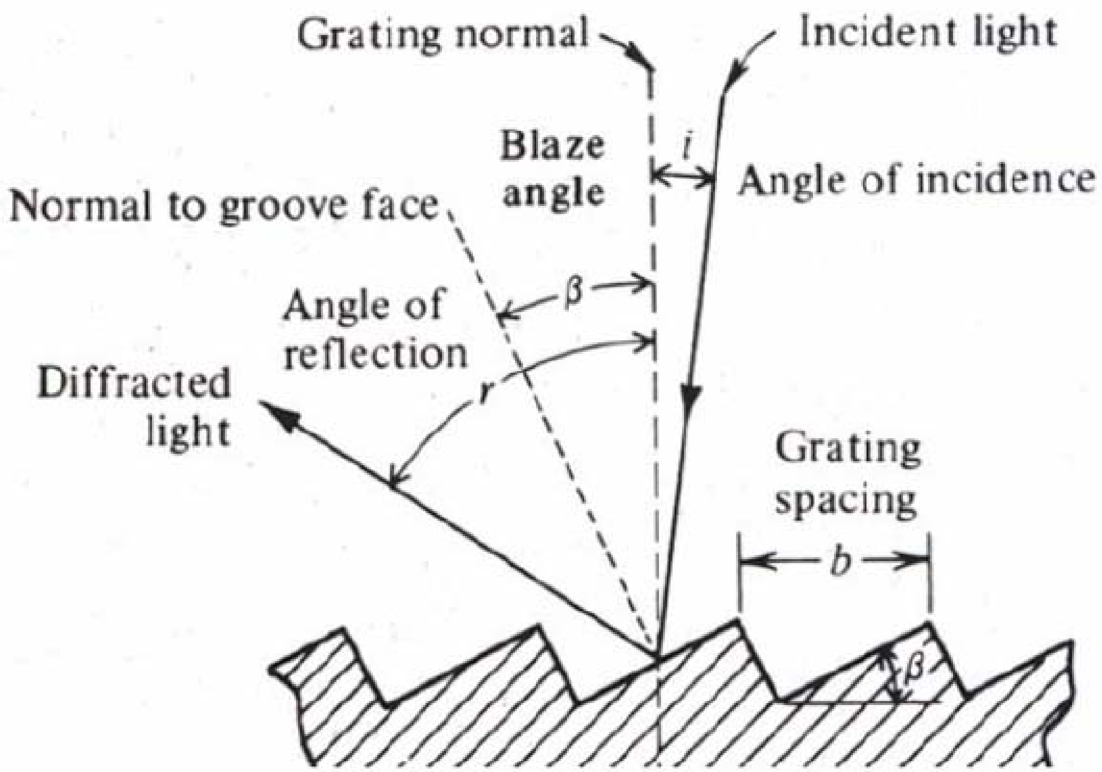
Grating Eqn.

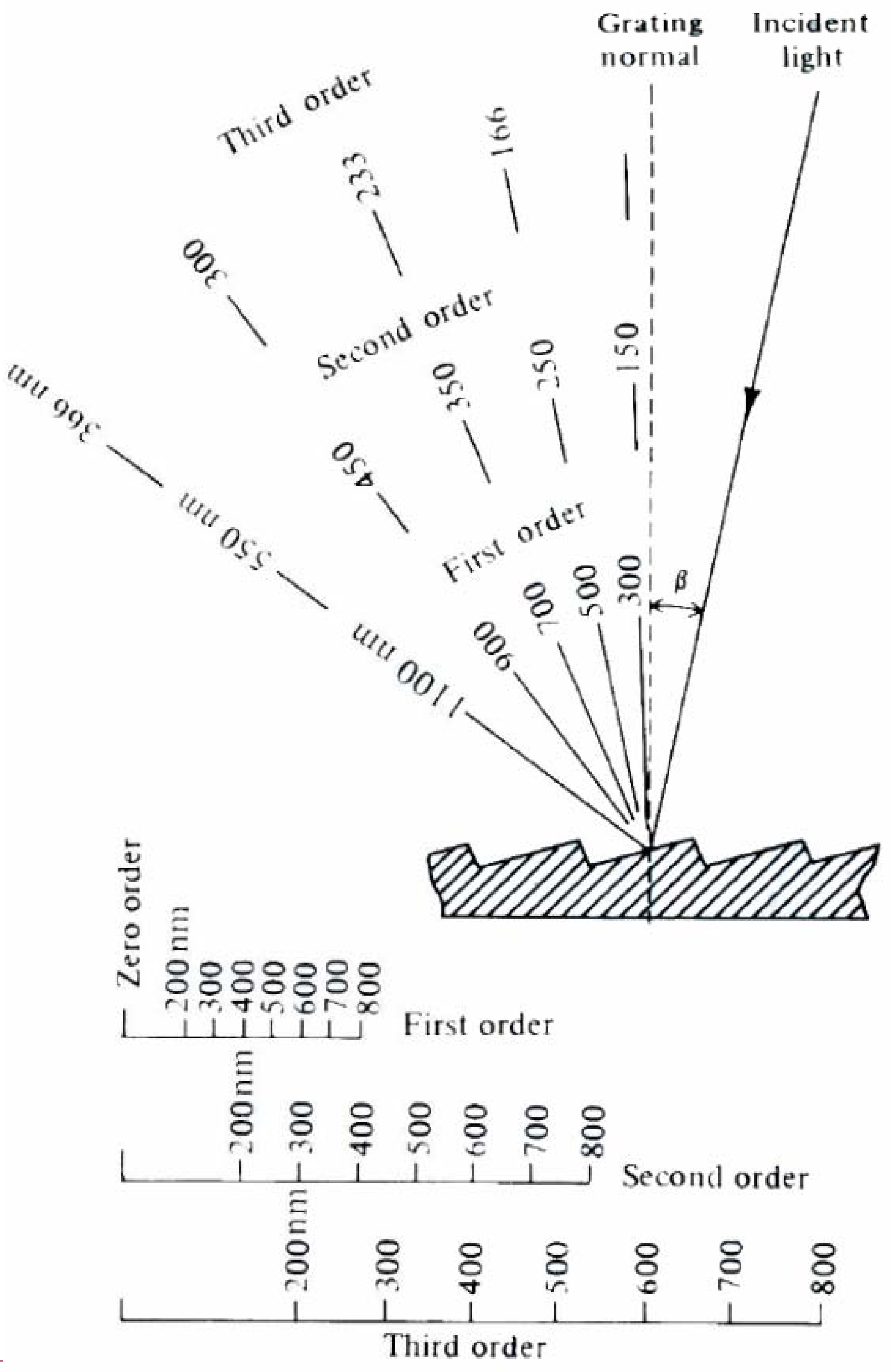


$$d(\sin\theta_m - \sin\theta_i) = m\lambda$$

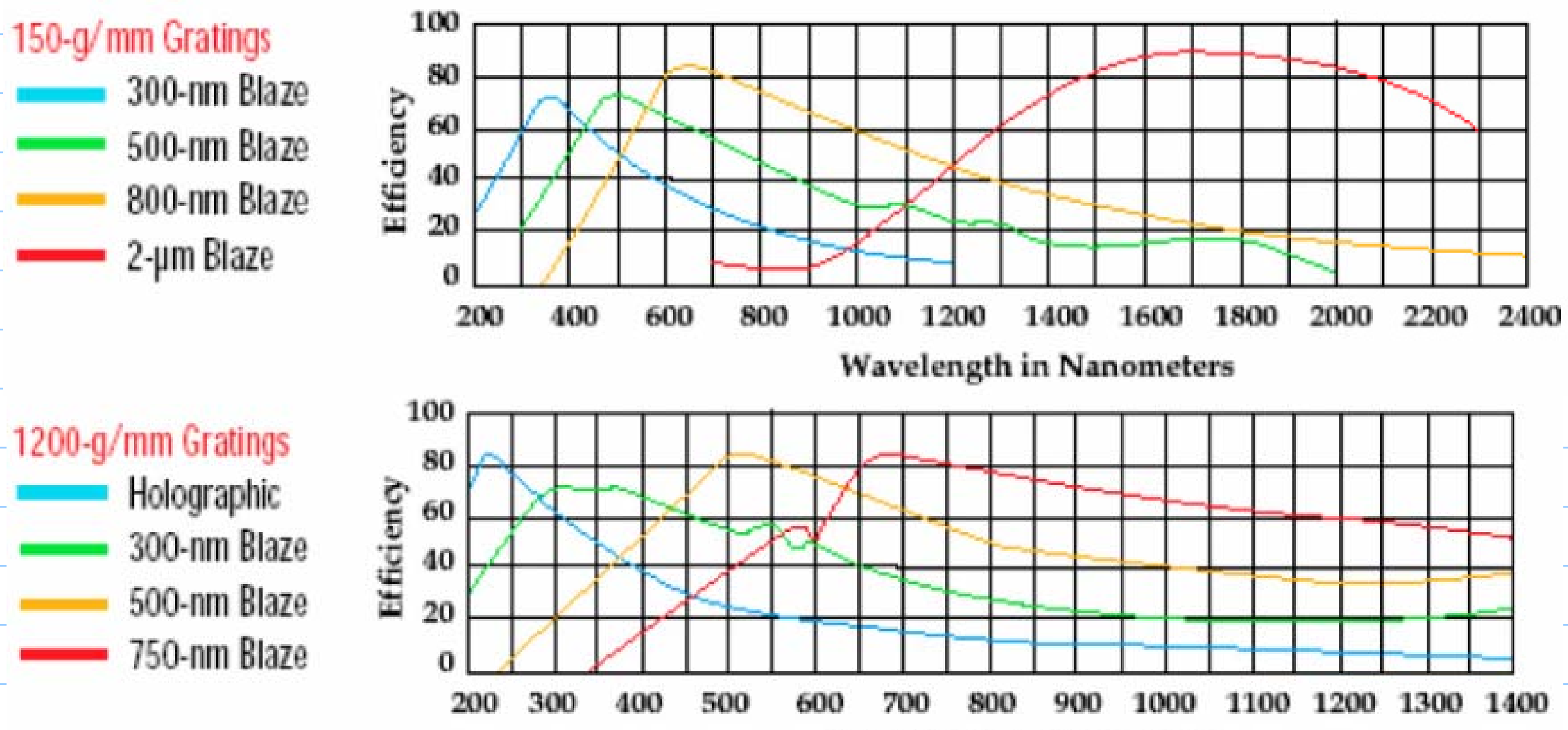
$$\theta_m = \sin^{-1}\left[\sin\theta_i + \frac{m\lambda}{d}\right]$$

Grating Introduction




Grating normal
Incident light
β
Third order
166
233
300
Second order
150
250
350
450
366 nm
550 nm
1100 nm
First order
900
700
500
300
Zero order
200 nm
300
400
500
600
700
800
First order
200 nm
300
400
500
600
700
800
Second order
200 nm
300
400
500
600
700
800
Third order

Gratings—Practical Considerations



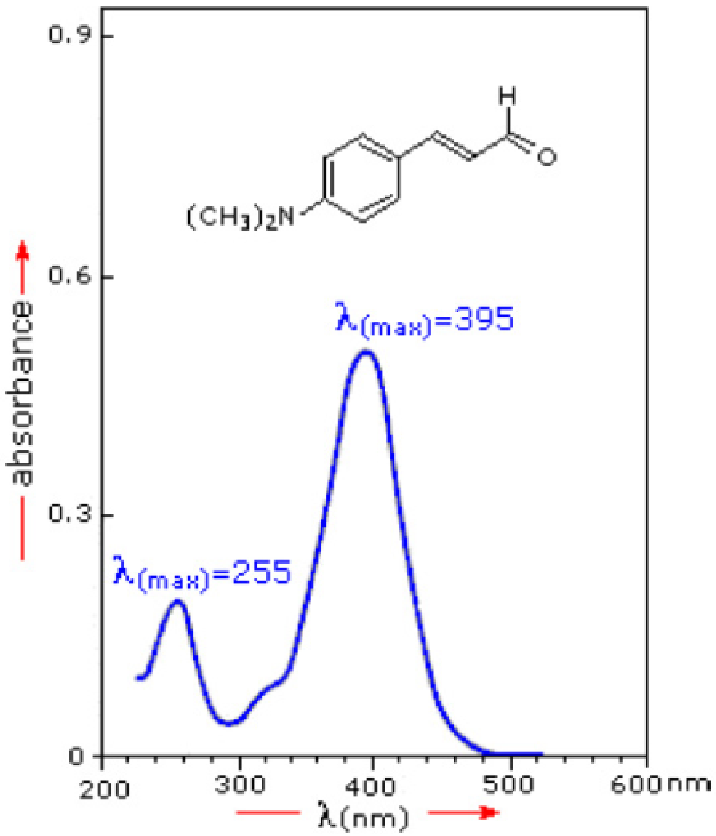
- Shorter wavelength → greater g/mm number
- Blazing wavelength can be specified

$$I = I_0 10^{-\epsilon c l}$$

c = concentration

l = length

$\epsilon > 10{,}000$ strong absorption



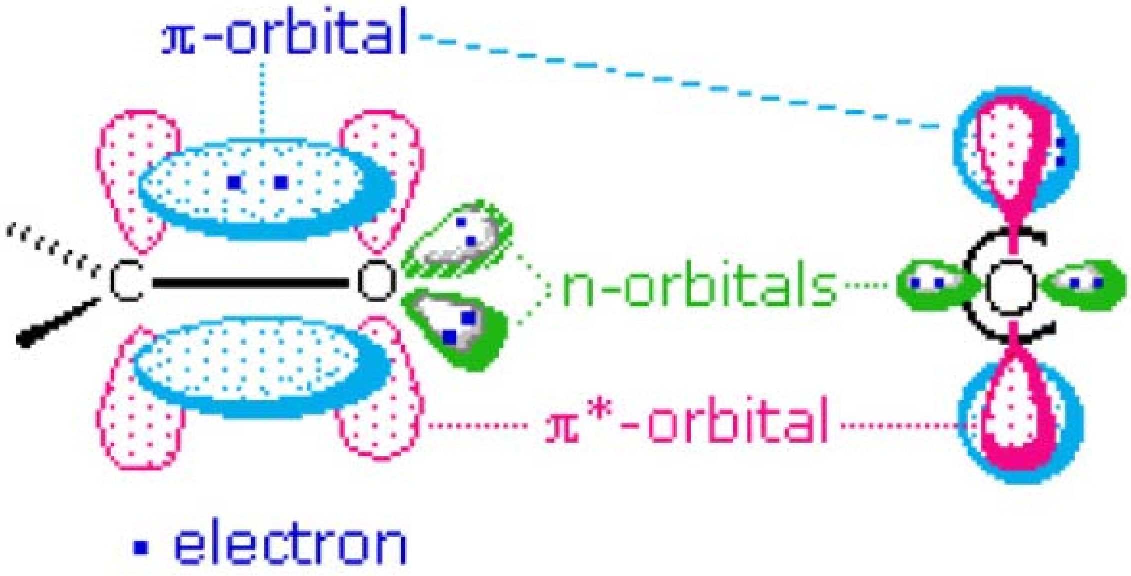
Extinction coefficient

$\epsilon = .87 \times 10^{20} P \cdot a$

$P =$ transition probability between
0 and 1

$a =$ chromophore area cm^2

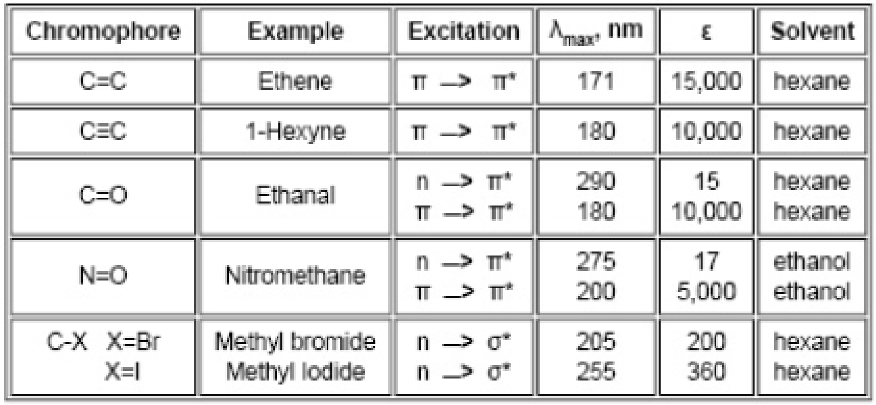
Isolated carbonyl group



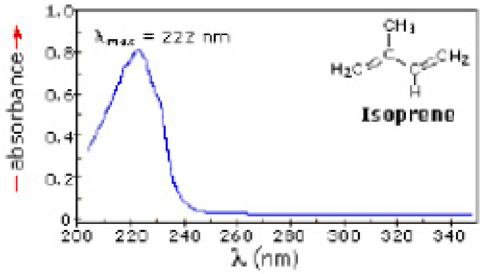
Poor overlap between $n \to \pi^*$

Good overlap $\pi \to \pi^*$

Chromophores

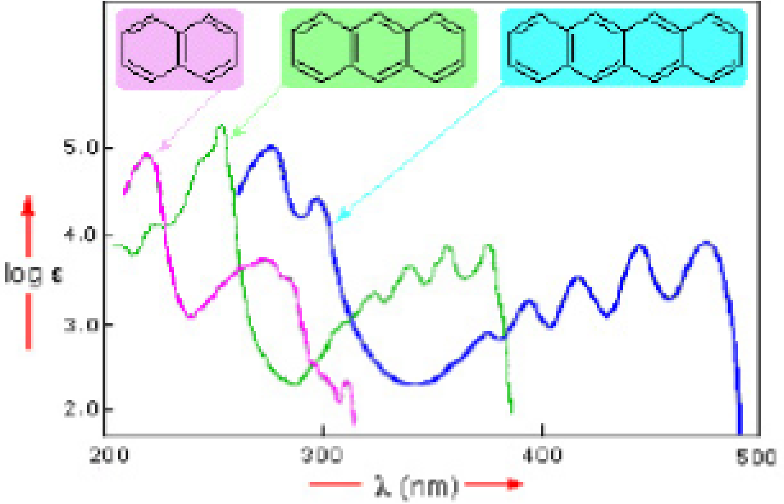


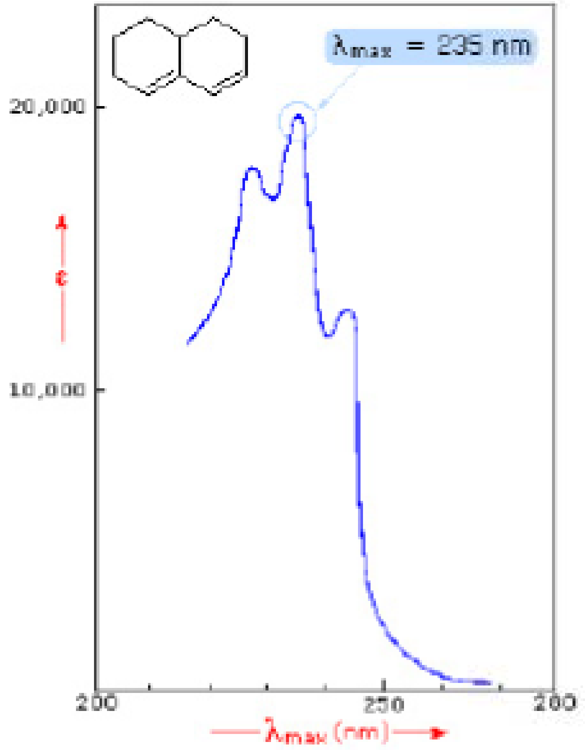
Chromophore	Example	Excitation	λ_{max}, nm	ε	Solvent
C=C	Ethene	$\pi \rightarrow \pi^*$	171	15,000	hexane
C≡C	1-Hexyne	$\pi \rightarrow \pi^*$	180	10,000	hexane
C=O	Ethanal	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	290 180	15 10,000	hexane hexane
N=O	Nitromethane	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	275 200	17 5,000	ethanol ethanol
C-X X=Br X=I	Methyl bromide Methyl Iodide	$n \rightarrow \sigma^*$ $n \rightarrow \sigma^*$	205 255	200 360	hexane hexane



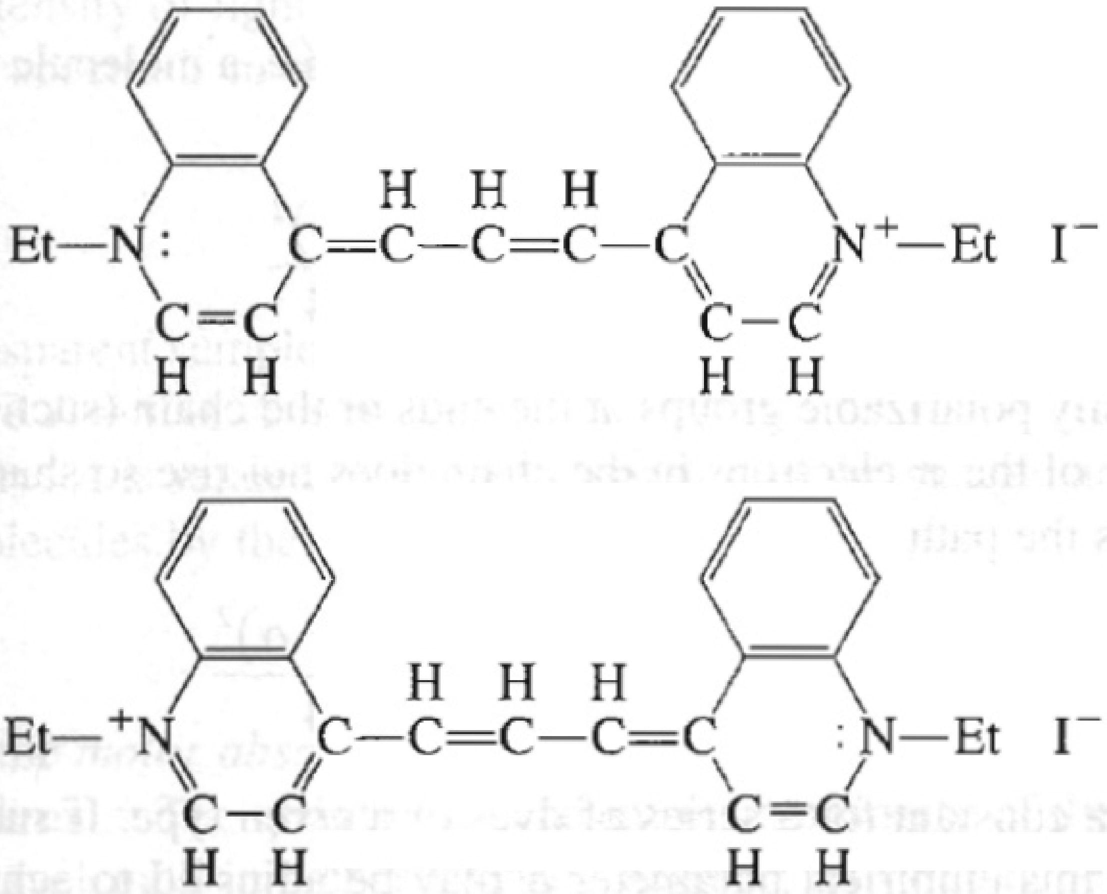
Influence of increased conjugation

napthalene anthracene tetracene





Cryptocyanine



Replace π electrons with a box of length L then

$$E_n = \frac{h^2 n^2}{8mL^2} \quad n = 1, 2, 3$$

Energy change with excitation by light

$$\Delta E = \frac{h^2}{8mL^2}(N+1)$$

Since

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

$$\lambda = \frac{8mc}{h} \frac{L^2}{N+1}$$

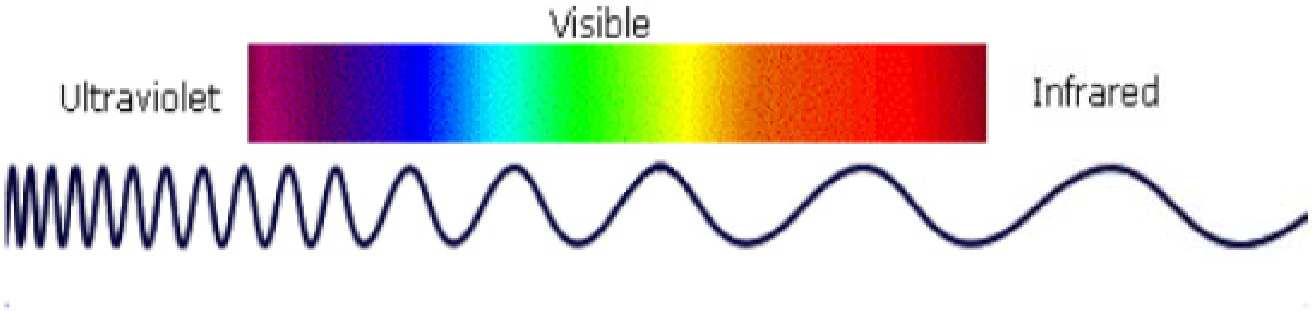
If the number of carbon atoms in the polymethine chain is p then N = p+3 where L is the length of chain between the nitrogen atoms plus a bond distance of each side

Thus $L = (P+3)\ell$ where ℓ is the bond length between atoms along the chain

$$\lambda = \frac{8mc\ell^2}{h} \frac{(P+3)^2}{P+4}$$

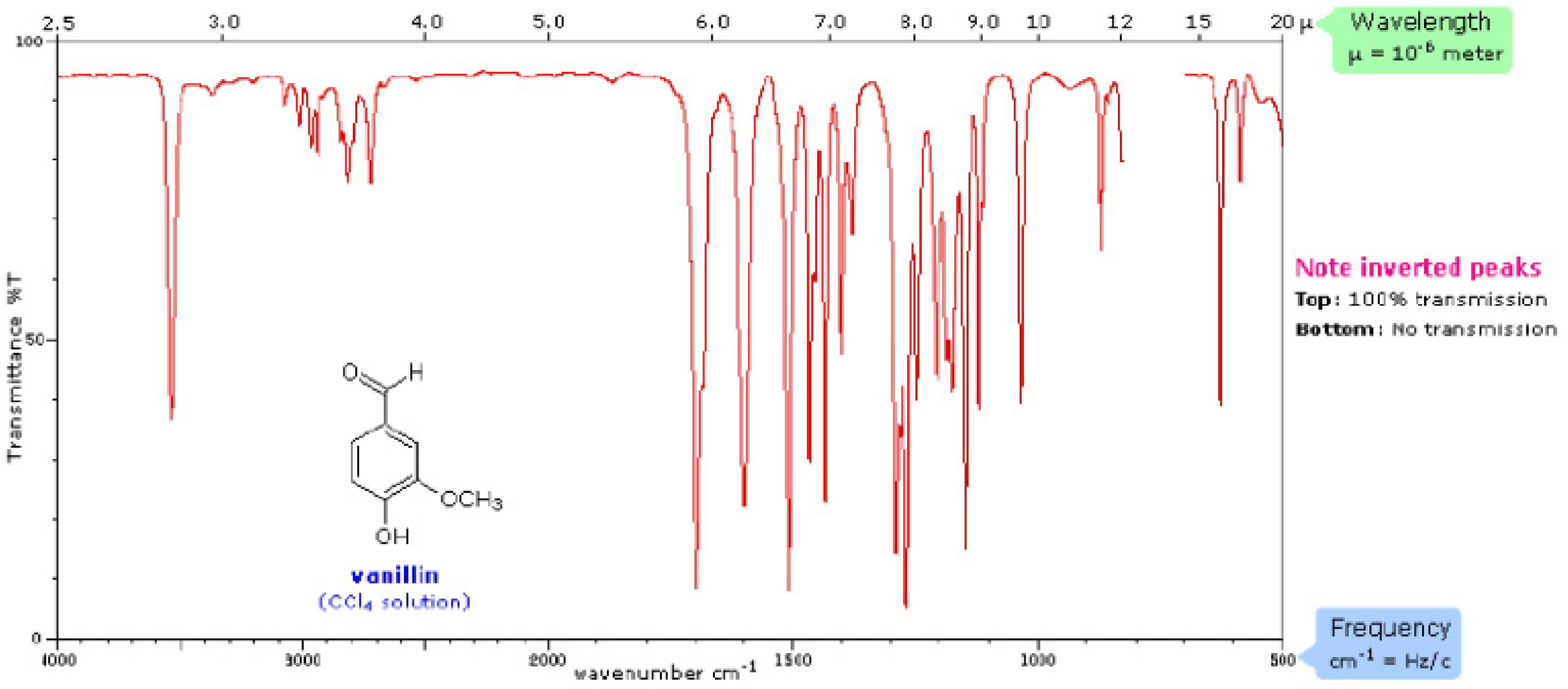
Thus λ will shift to the red with increasing P

Infrared Spectroscopy



Infrared 2.5μ to 16 μ

Typical IR Spectra



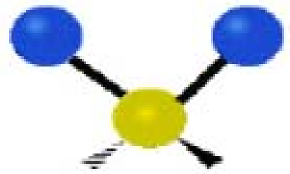
vanillin
(CCl_4 solution)

Note inverted peaks

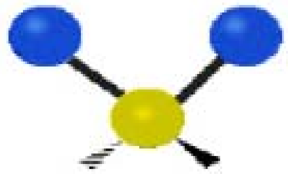
Top: 100% transmission

Bottom: No transmission

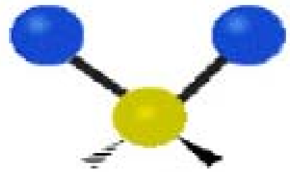
Vibrational Modes



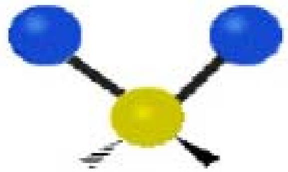
symmetrical stretching



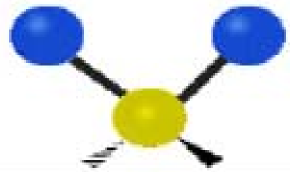
asymmetrical stretching



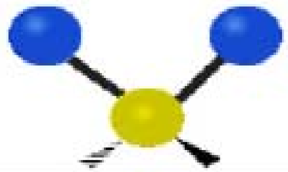
scissoring



rocking

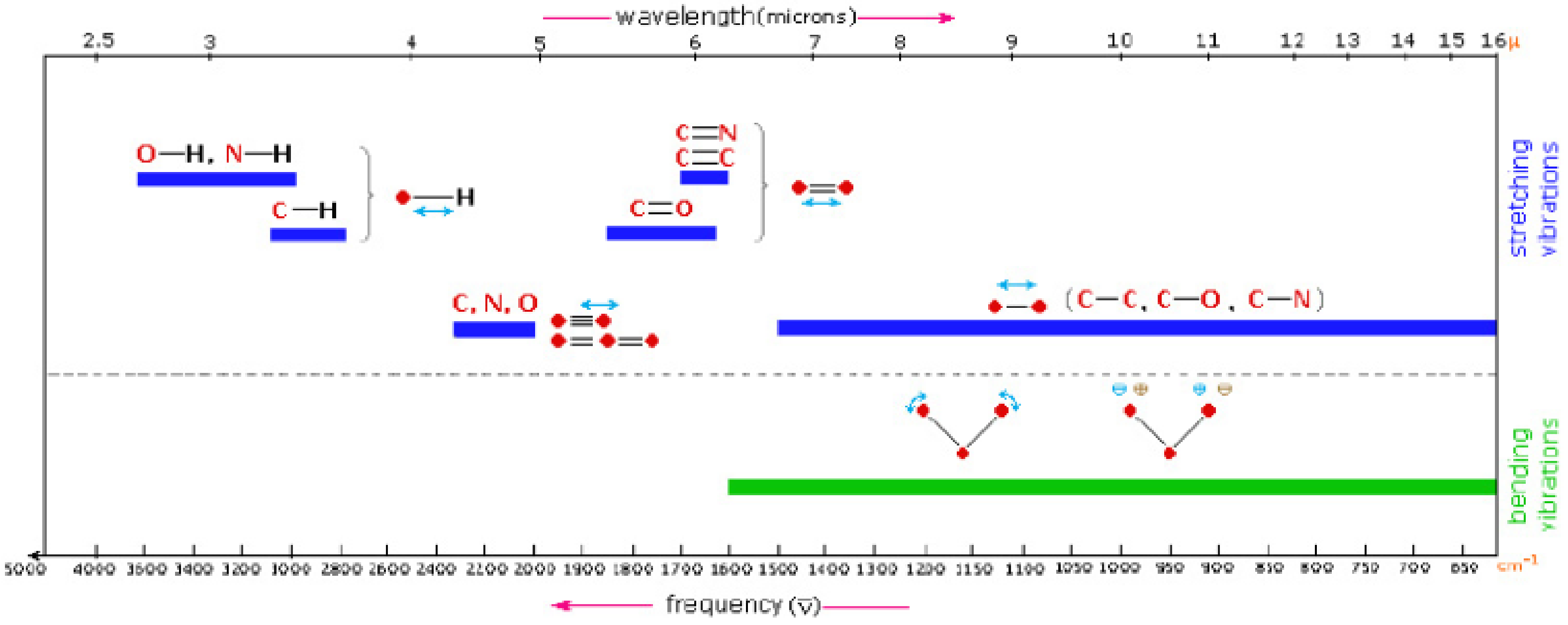


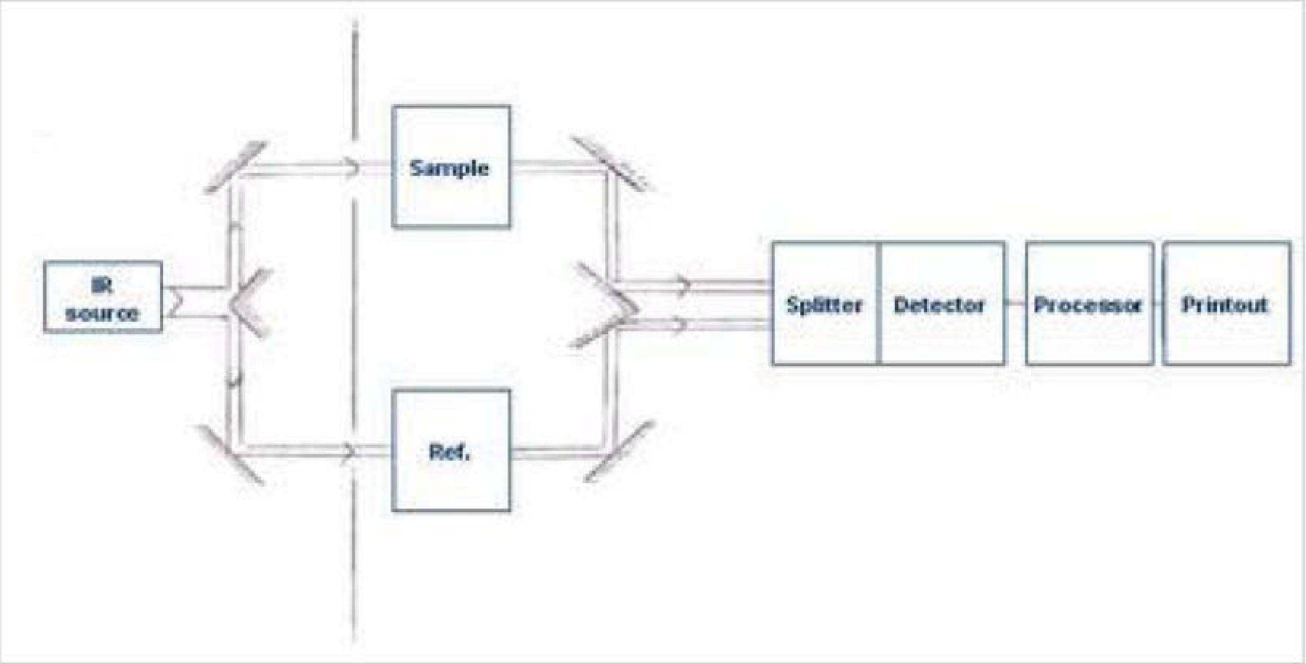
wagging



twisting

Modes and IR Spectrum

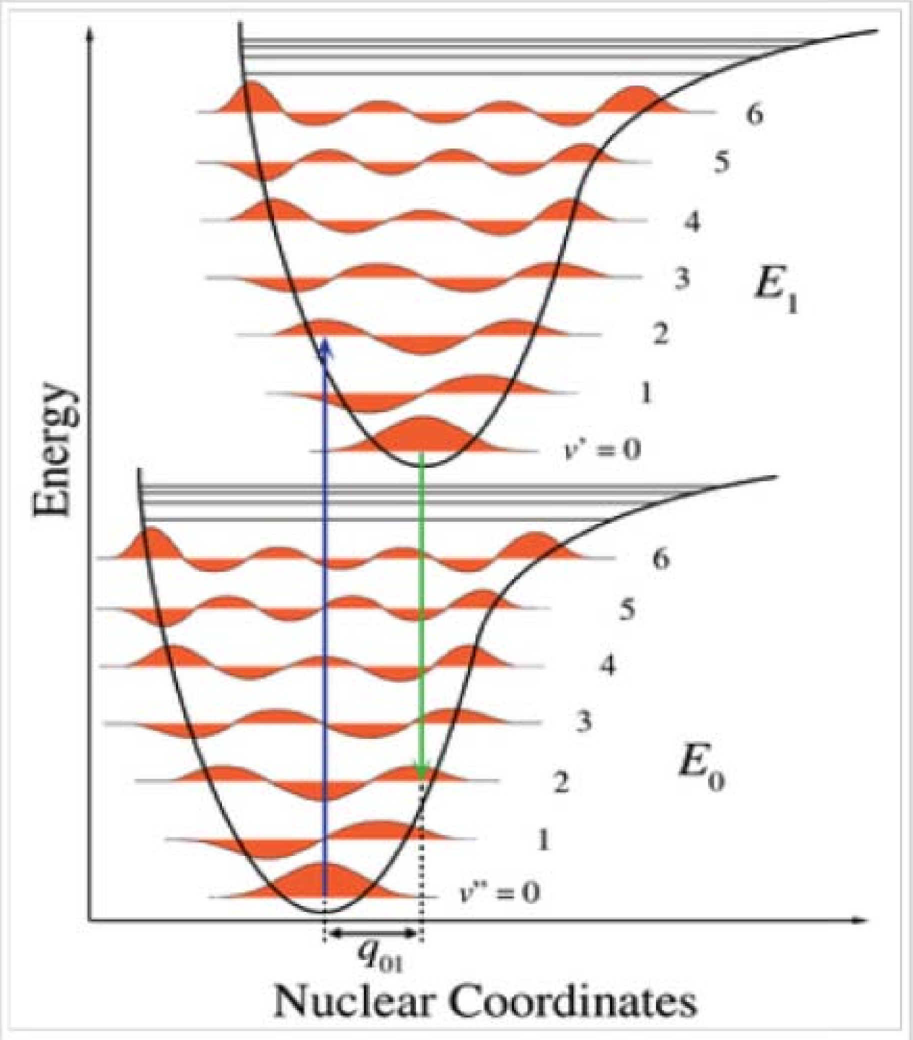


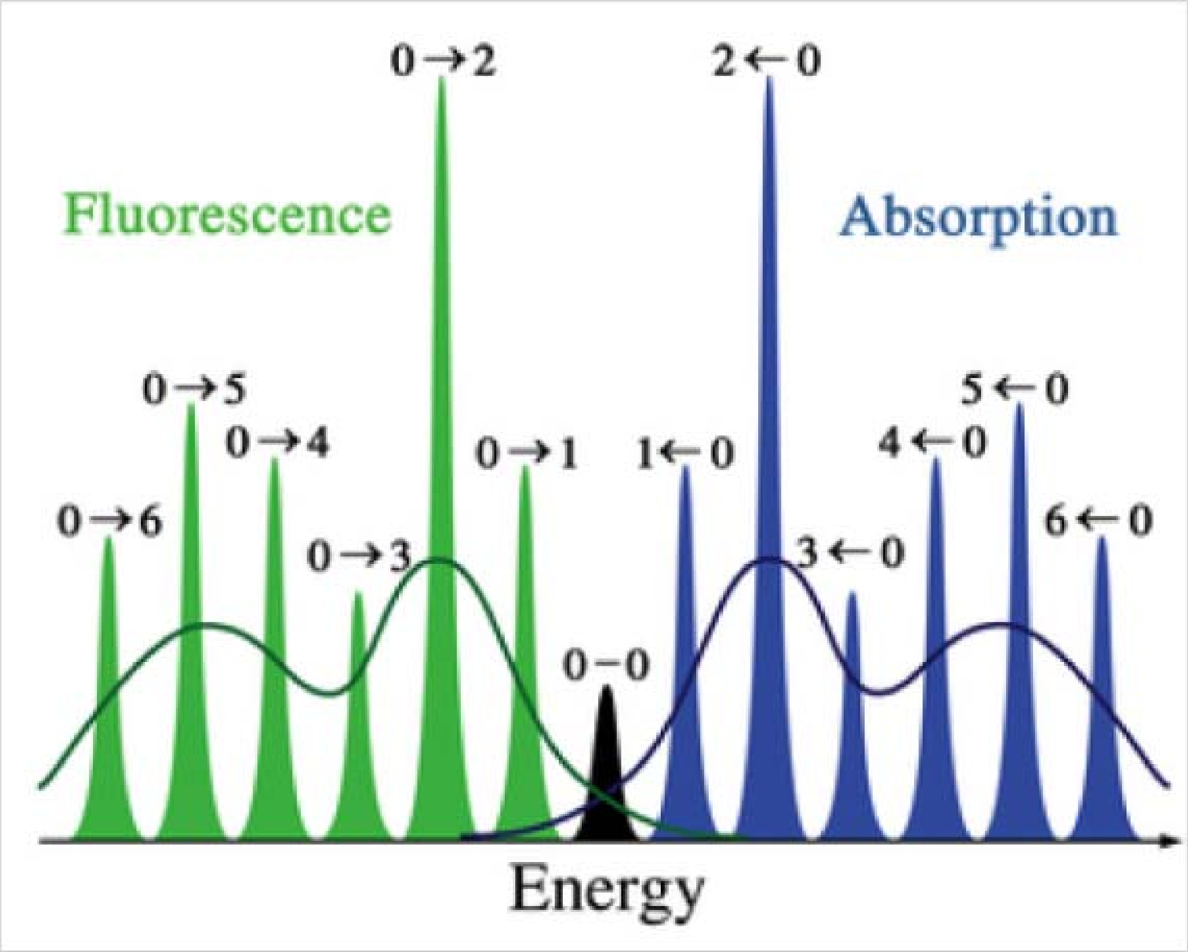


Typical apparatus

Franck-Condon Principle

Vibronic Transitions




0→2
2←0
Fluorescence
Absorption
0→5
0→4
0→1
1←0
4←0
5←0
0→6
6←0
0→3
3←0
0–0
Energy