Introduction to Spectroscopy

Spectroscopy: the study of the molecular changes induced by the interaction of chemical compounds with various regions of the electromagnetic spectrum.

The Electromagnetic Spectrum:

The Relationship Between Wavelength, Frequency and Energy:

Wavelength and frequency are inversely related by the equation

$$\lambda = \frac{c}{\nu}$$

where λ= wavelength in cm

c = speed of light (2.998 x10^{10} cm/sec)

ν= frequency in hertz

As noted in the figure above, the electromagnetic spectrum is arbitrarily divided into various regions, with the familiar visible region accounting for only a small portion of the overall spectrum (from 3.8 x 10^{-5} cm to 7.8 x 10^{-5} cm).
Electromagnetic energy is transmitted only in discrete energy packets, or quanta, where the amount of energy corresponding to 1 quantum of energy (or 1 photon) of a given frequency is expressed by the equation

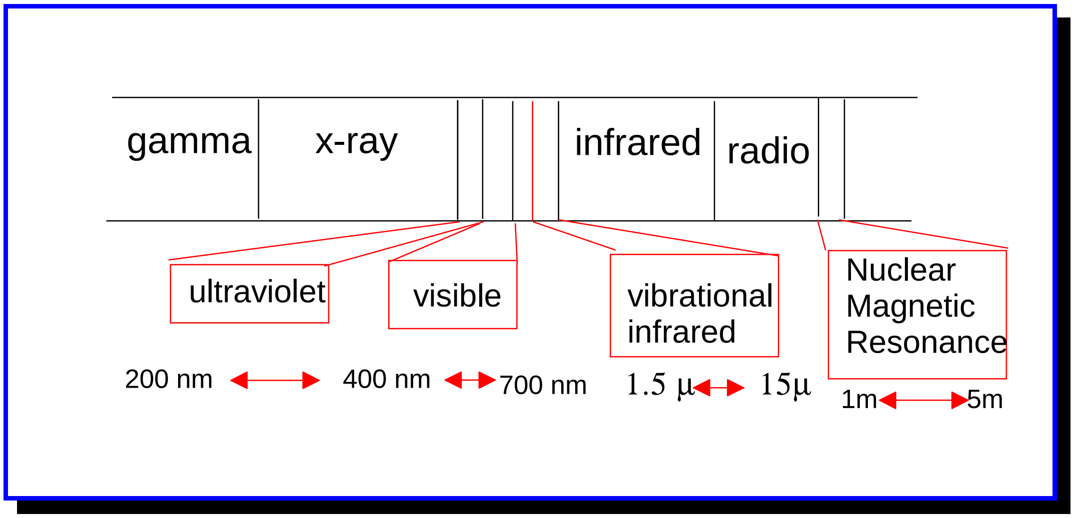
$$E = h\nu = \frac{hc}{\lambda}$$

where E = the energy of 1 photon

h = Planck's constant (6.626 x 10^{-34} J/s)

ν = wavelength in cm

Regions of the Electromagnetic Spectrum that are most useful for the Structural Determination of Chemical Compounds



Types of Molecular Changes that Result from the Interactions of Chemical Compounds with Various Regions of the Electromagnetic Spectrum.

Region of Spectrum	Molecular Change	Energy kcal/mol	Frequency Hz	Wavelength cm
ultraviolet	electronic Transitions	100	10^{15}	$2x10^{-5}$ -- $4x10^{-5}$
visible	electronic	50	$5x10^{14}$	$4x10^{-8}$ -- $7x10^{-5}$
Infrared	molecular vibrations	5	10^{13} -- 10^{14}	10^{-4} -- 10^{-2}
microwave	molecular rotations	$3x10^{-3}$	$3x10^{10}$	1
radio	orientation of spin of nucleus in magnetic Field	10^{-7}	10^{6}	5 x 10^{5}

Structural Information obtained about Chemical Compounds from Various Forms of Spectroscopy

Ultraviolet-visible Spectroscopy (UV-VIS) - presence and nature of conjugated pi electron systems

Mass Spectroscopy (MS) - molecular size and formula

Infrared Spectroscopy (IR) - functional (reactive) chemical groups present

Nuclear Magnetic Resonance Spectroscopy (NMR) - carbon-hydrogen framework of molecules

Ultraviolet - Visible Spectroscopy

1. What portion of the electromagnetic spectrum constitutes the ultraviolet-visible region?

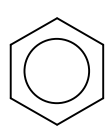
   UV goes from 200 nm to 400 nm

   VIS goes from 400 nm to 700 nm

2. What must a molecule possess to absorb radiation in this region of the spectrum?

   Chromophores -- distinctive bonding arrangements with electrons that are easily excited, usually conjugated double bonds, double bonds conjugated with carbonyl groups, or aromatic rings.

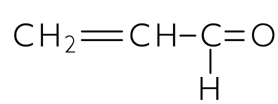
   Examples:



Benzene

$CH_2{=}CH{-}CH{=}CH_2$

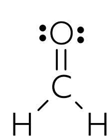
Butadiene



Acrolein (propenal)

3. What happens when chromophores of a molecule absorb ultraviolet or visible radiation?

   Excitation of electrons from a ground state to an excited state.
   For example:



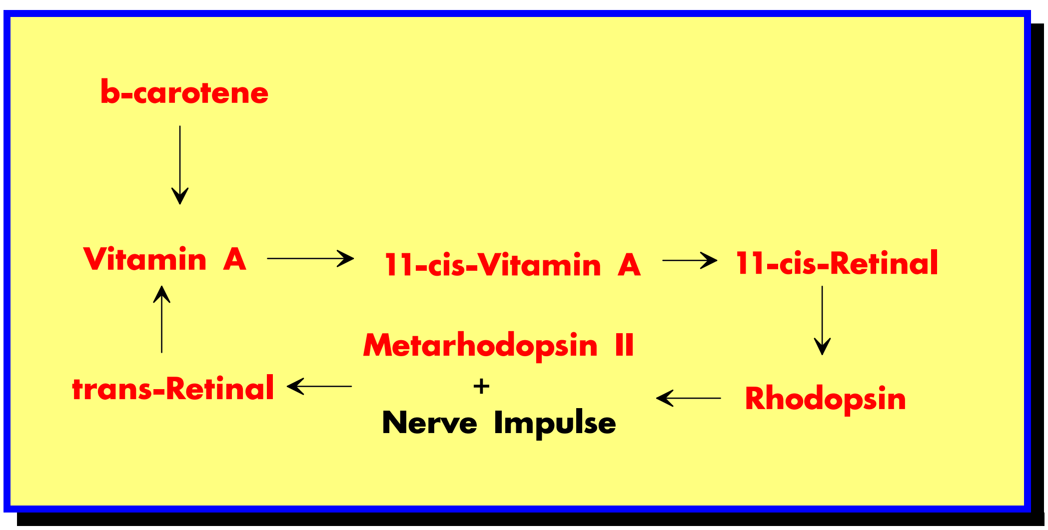
4. How do we measure the absorption of ultraviolet of visible radiation by chromophores in a molecule?

5. What does the ultraviolet-visible absorption spectrum of a molecule look like?

6. Why is the absorption band broad (occurs over a relatively wide wavelength range)?

7. What is the relationship between the structure of the molecule and the wavelength where maximal absorption occurs?

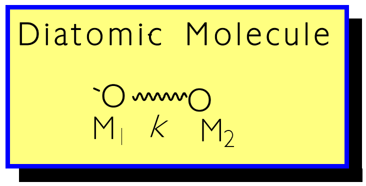
8. A biological example illustrating the role of the absorption of visible light in vision.
β-carotene -- its structure and ultraviolet-visible absorption spectrum



The visual cycle: the actual series of events is more complicated than the diagram indicates, involving several intermediate steps in the light-induced conversion of rhodopsin into metarhodopsin II

An Introduction to Infrared Spectroscopy

The wavelength, or wavenumber of infrared light absorbed corresponds to frequencies of molecular vibrations.



k is the force constant, the variable which characterizes the stiffness of the spring. If *k* is large the spring is a strong one, if *k* is small the spring is weak.

The diatomic molecule vibrates with the frequency

$$\upsilon = \sqrt{\frac{k}{\mu}} \div 2\pi$$

The frequency depends both on the force constant *k* and the reduced mass μ

μ is the **reduced mass**, defined as $(M_1 + M_2)/(M_1 \times M_2)$. The reduced mass is the effective mass on which the spring actually acts.

As <u>k</u> increases the vibrational frequency increases
As μ increases the vibrational frequency decreases

The energy of a vibration is given by

$$E = h\upsilon(n + \tfrac{1}{2})$$

Where n is any integer and h is called Planck's Constant.

The energy of a photon, a particle of light, is given by $E = h\upsilon$
Where ν is the frequency of the light.

Light is absorbed by a diatomic molecule when the energy of the light, $h\nu$, is the same as the difference in energy between two of the vibrational energy levels, $h\nu$. The frequency of the light absorbed, therefore, is the same as the vibrational frequency.

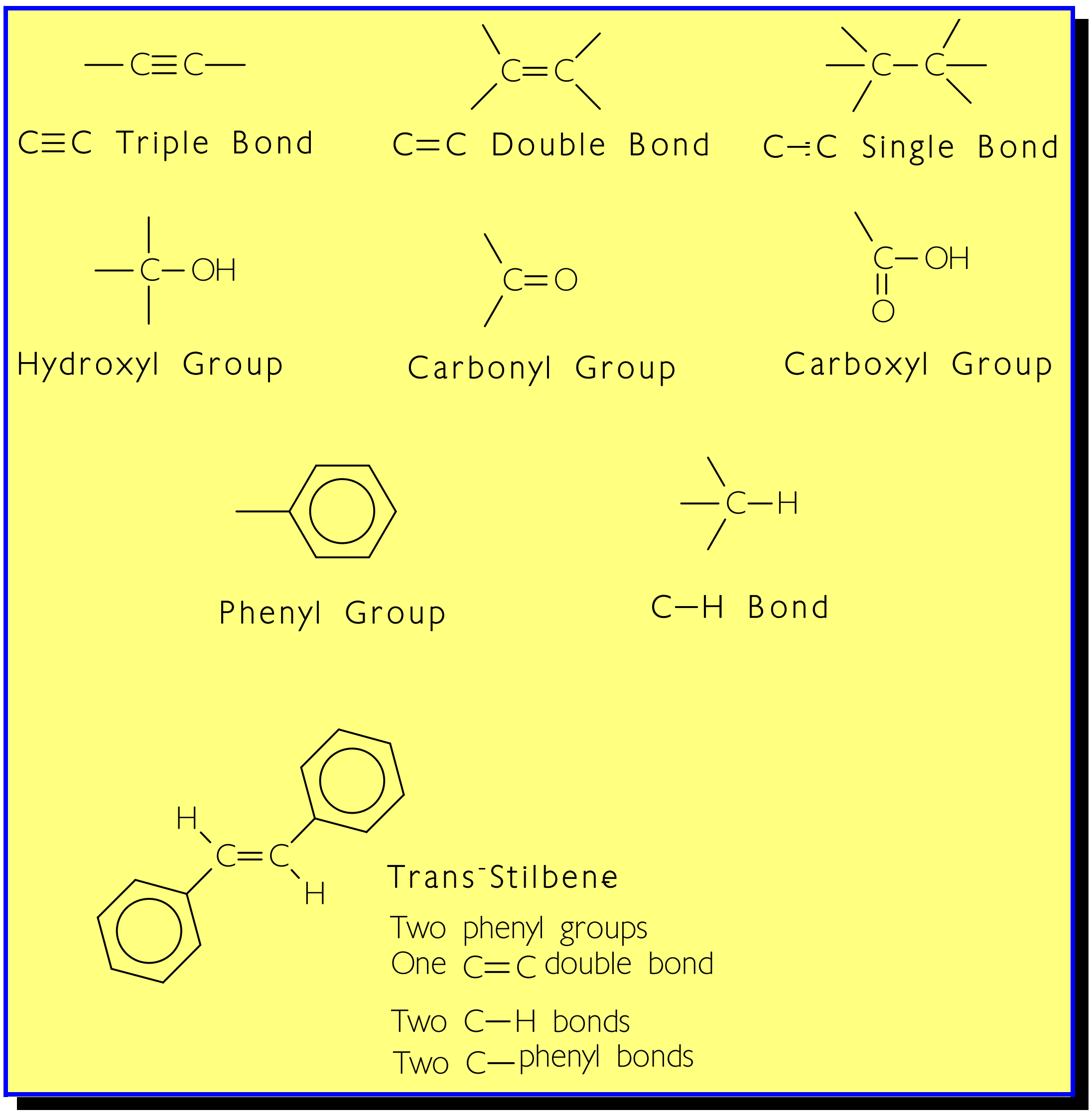
This also yields the wavelength of the light absorbed since wavelength and frequency are related by

$$\lambda = \frac{c}{\nu}$$

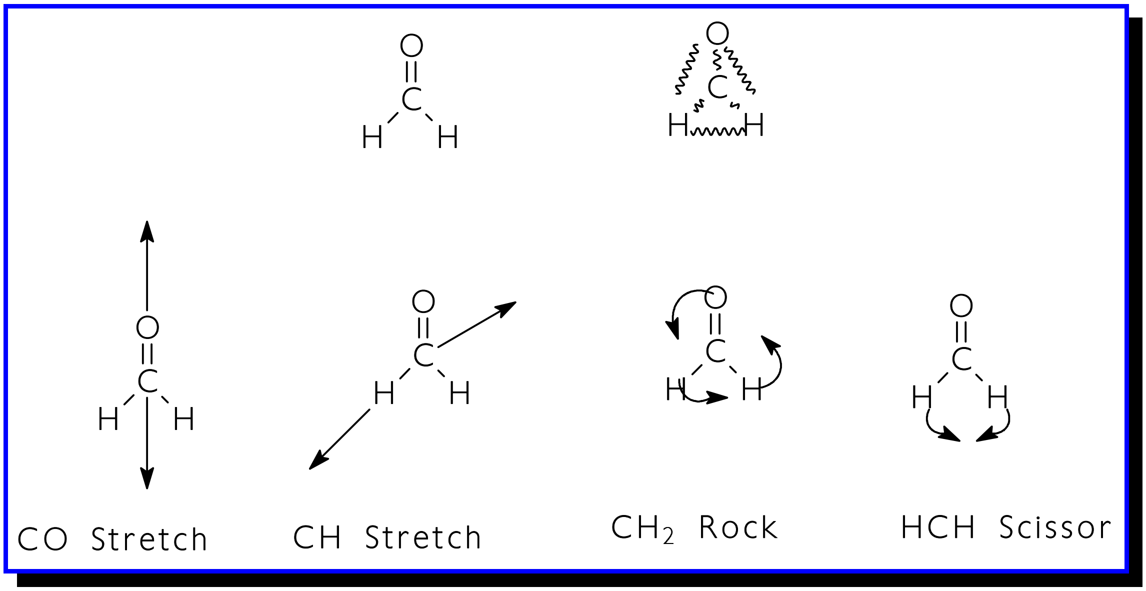
Where **c** is the speed of light.

Infrared Spectroscopy in the Analysis of Organic Molecules

Organic molecules can be constructed from basic functional groups.



Picture Polyatomic Molecules as being a collection of masses connected by springs that can show more than one vibration.
Each vibration of a polyatomic molecule has a characteristic reduced mass and a characteristic force constant.



Therefore, each vibration of a polyatomic molecule has a characteristic wavenumber.

Formaldehyde:	CH stretch	2820 cm^{-1}
	CO stretch	1746 cm^{-1}
	CH scissor	1500 cm^{-1}
	CH rock	1249 cm^{-1}