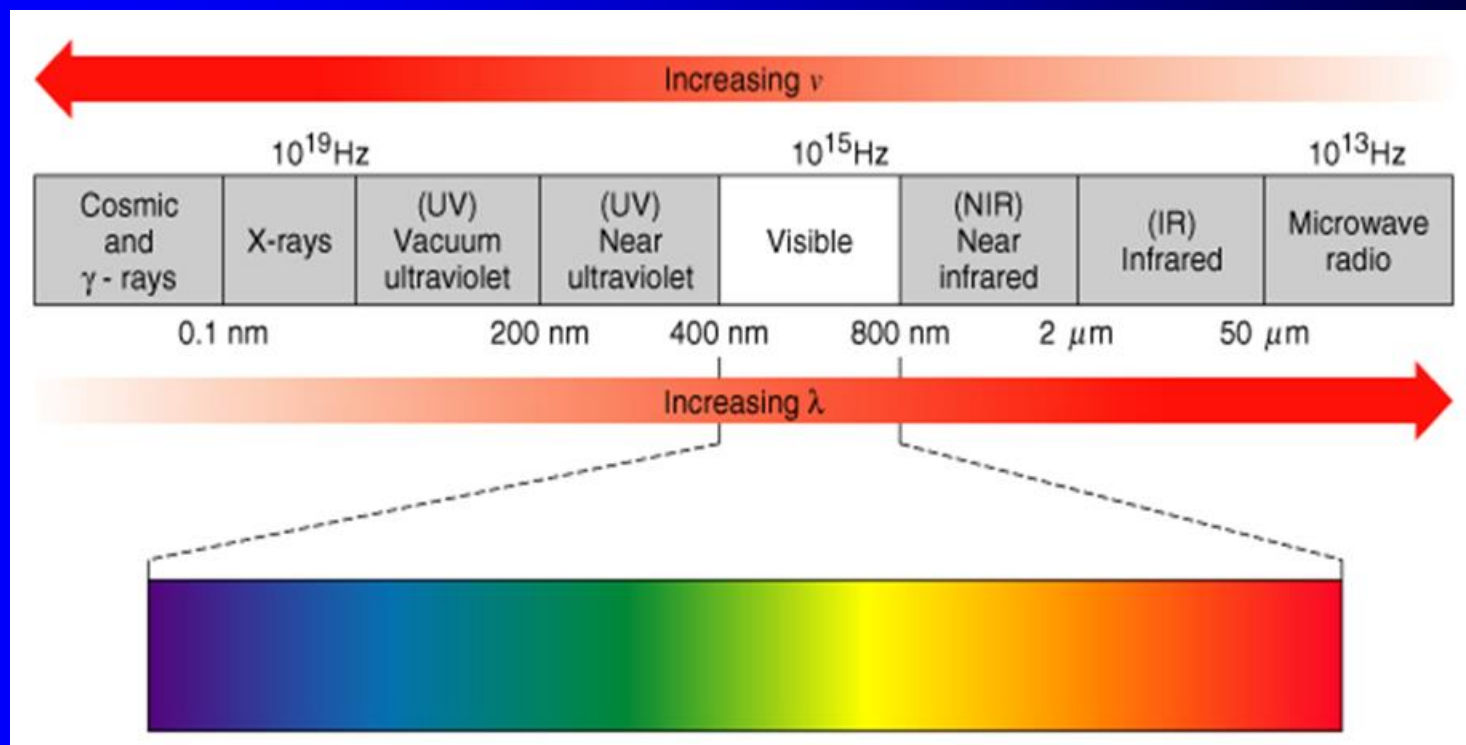


Lecture 7

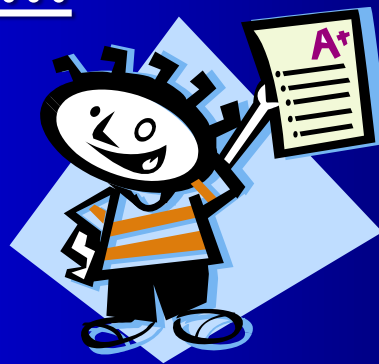
UV-Vis spectroscopy



First Midterm Exam

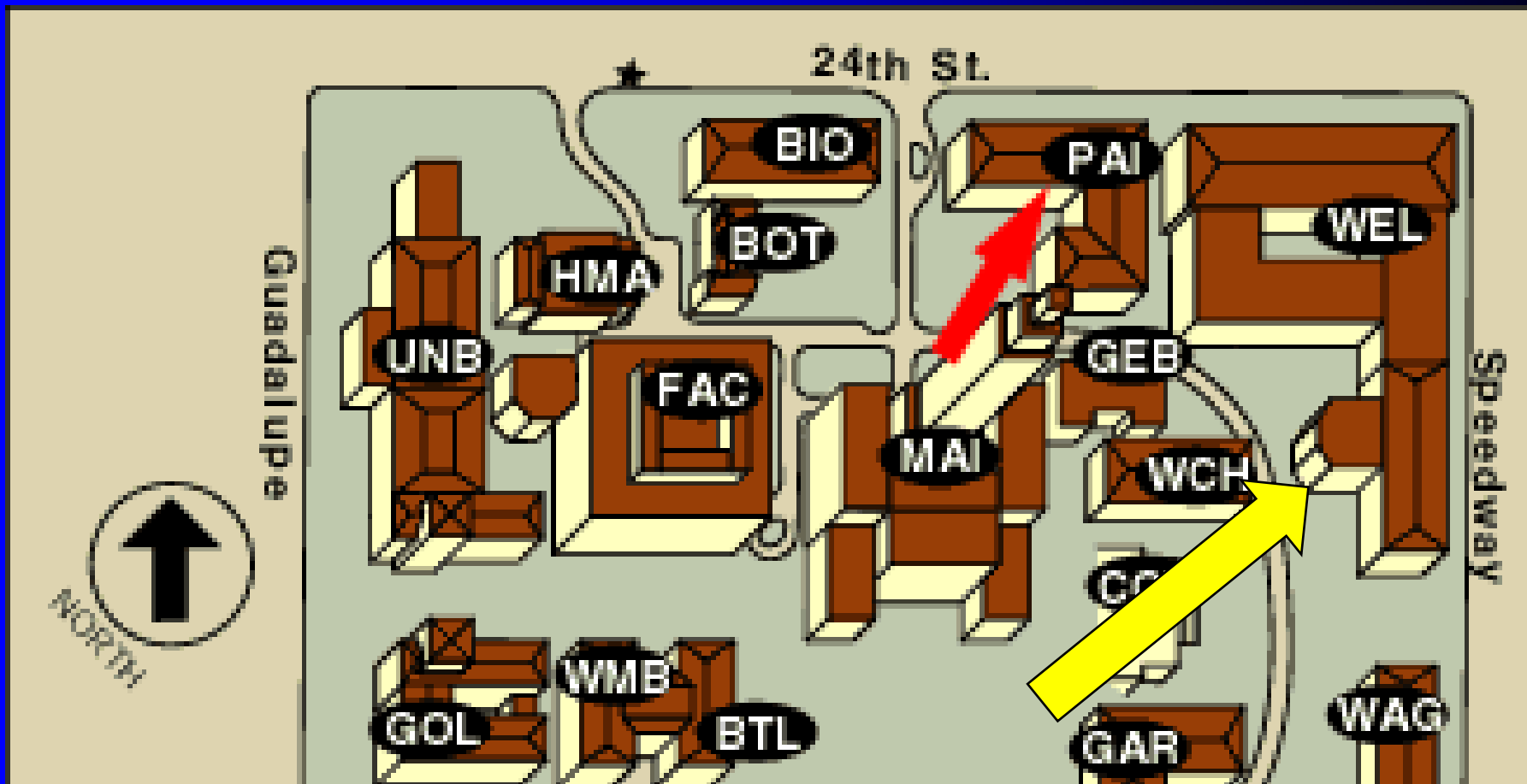
- When: Wednesday, 2/17
- When: 7-9 PM (please do not be late)
- Where: WEL 3.502...see next slide!!!
- What: Covers material through Thursday's lecture
- Remember: Homework problems!!
- Practice: Old exams will be posted on the web site
- Review Sessions: Mon & Tues 5-6 in room TBA
- Please...bring pencils, an eraser and a calculator only andDo a good job!!!

I will bother you! 😊



WEL 3.502

You can only enter from Inner Campus Drive!!!

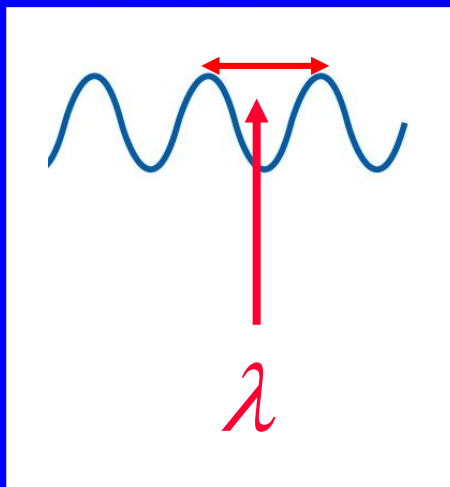


Mr Hooke says:

- The **position** (frequency) of the absorption of a stretching vibration depends on
 - the strength of the vibrating bond (*direct*) and
 - the masses of the atoms (*inverse*)
- The stronger the bond and the lighter the atoms connected by that bond, the higher the frequency (wavenumber) of the vibration
- The **intensity** of absorption depends primarily on the polarity of the vibrating bond



THE ENERGY OF ELECTROMAGNETIC WAVES



$$c = \lambda \nu \quad \bar{\nu} = \frac{1}{\lambda}$$

- $\bar{\nu}$ • (nu-bar) represents wavenumber, the number of wavelengths in 1 cm
- This is a unit of frequency!
- units are 1/cm or cm^{-1} (Kaysers)

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

$$10 \text{ microns (micrometers)} = 1000 \text{ cm}^{-1}$$



Infrared Absorption Frequencies

Structural unit	Frequency, cm^{-1}
-----------------	-----------------------------

Stretching vibrations (single bonds)

sp C—H	3310-3320
----------	-----------

sp^2 C—H	3000-3100
------------	-----------

sp^3 C—H	2850-2950
------------	-----------

sp^2 C—O	1200
------------	------

sp^3 C—O	1025-1200
------------	-----------

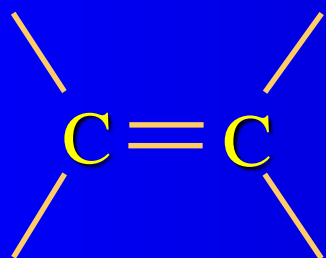


Infrared Absorption Frequencies

Stretching vibrations (multiple bonds)

Structural unit

Frequency, cm^{-1}



1620-1680



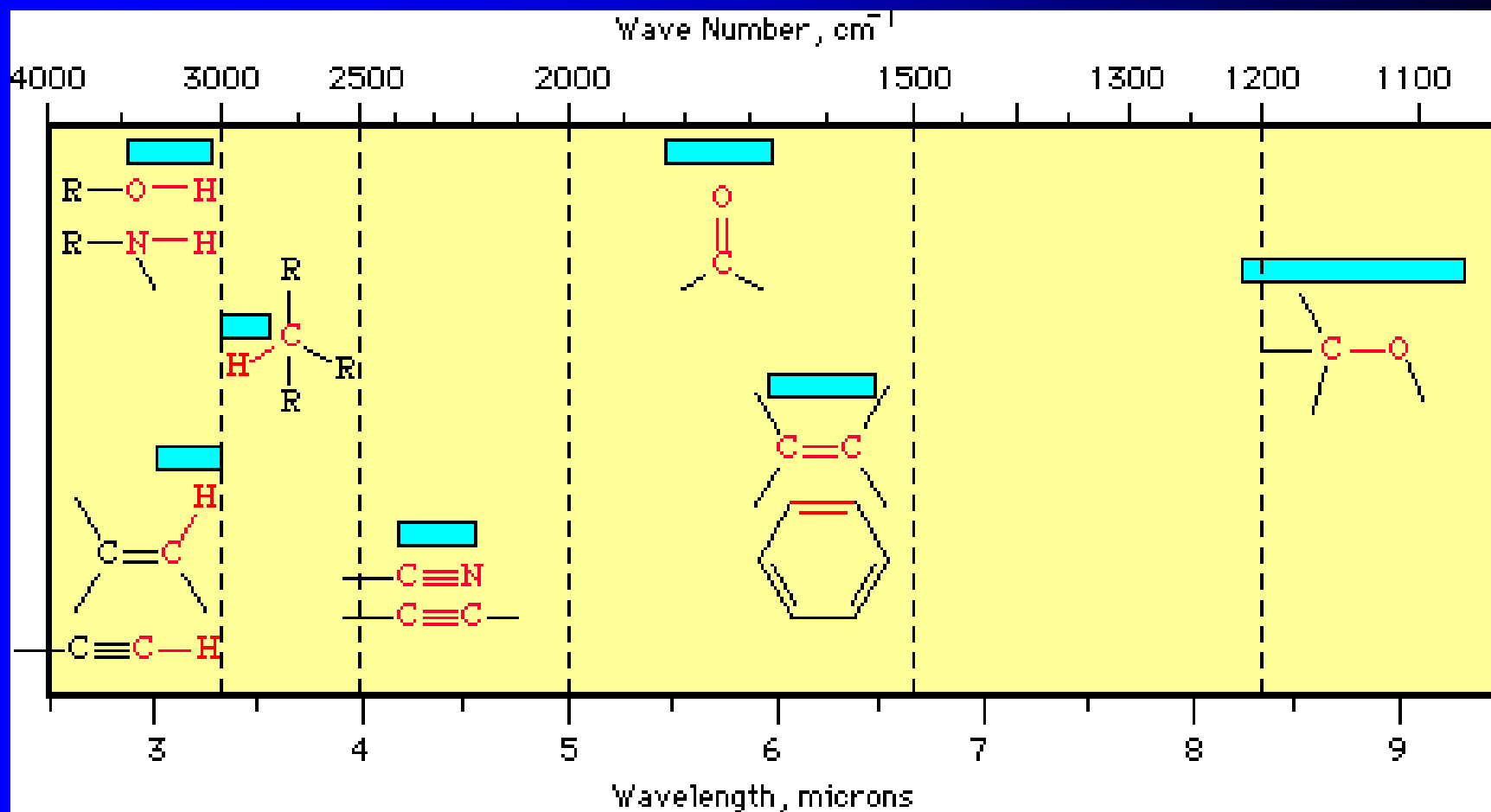
2100-2200



2240-2280



IR Group Correlation Tables



IR Group Correlation Tables

- Characteristic IR absorptions for some of the functional groups we deal with most often

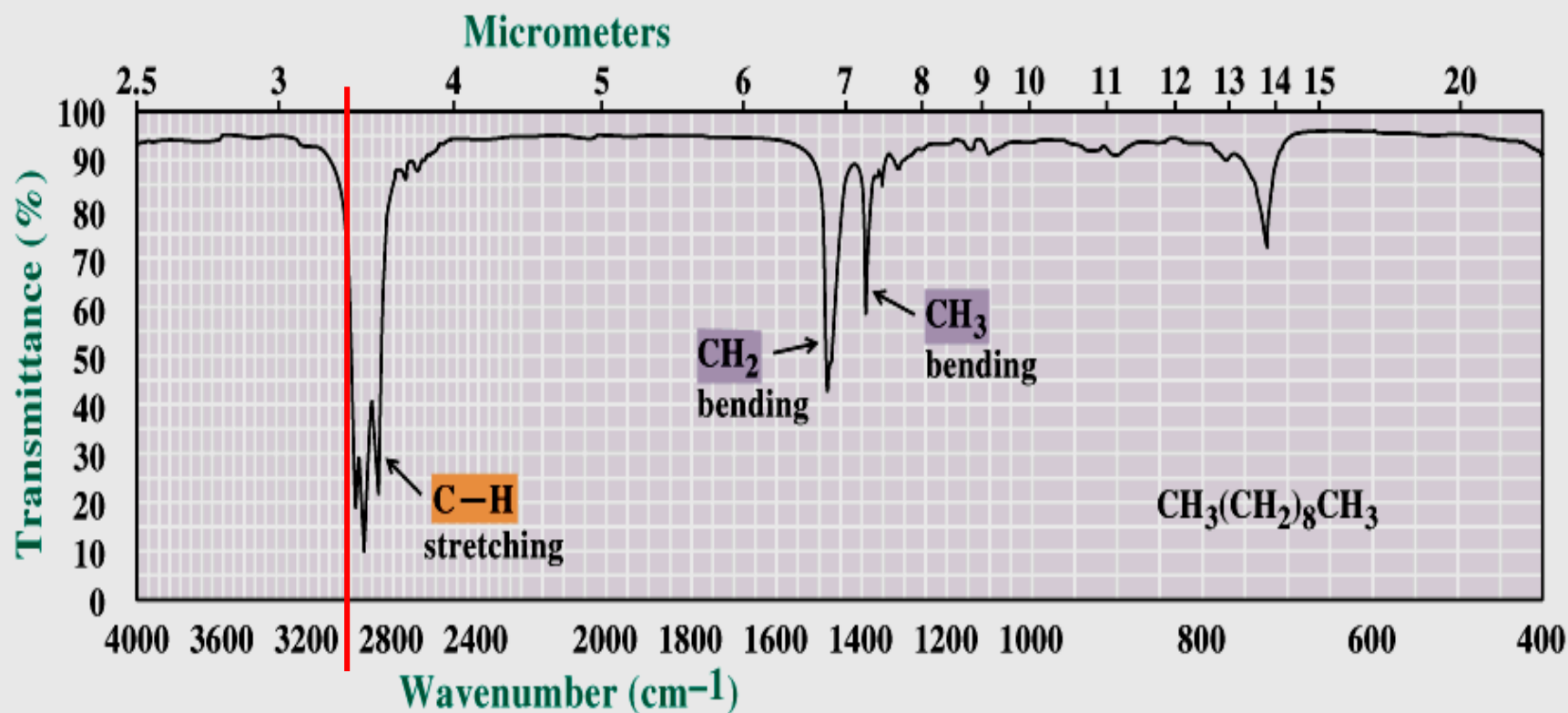
Bond	Frequency (cm ⁻¹)	Intensity
O-H	3200-3650	strong and broad
N-H	3100-3500	medium
C-H	2850-3300	medium to strong
C=O	1630-1810	strong
C=C	1600-1680	weak
C-O	1050-1250	strong



Hydrocarbon	Vibration	Frequency (cm⁻¹)	Intensity
<u>Alkane</u>			
C-H	stretching	2850 - 3000	strong
CH₂	bending	1450	medium
CH₃	bending	1375 and 1450	weak to medium
<u>Alkene</u>			
C-H	stretching	3000 - 3100	weak to medium
C=C	stretching	1600 - 1680	weak to medium
<u>Alkyne</u>			
C-H	stretching	3300	medium to strong
C≡C	stretching	2100-2250	weak

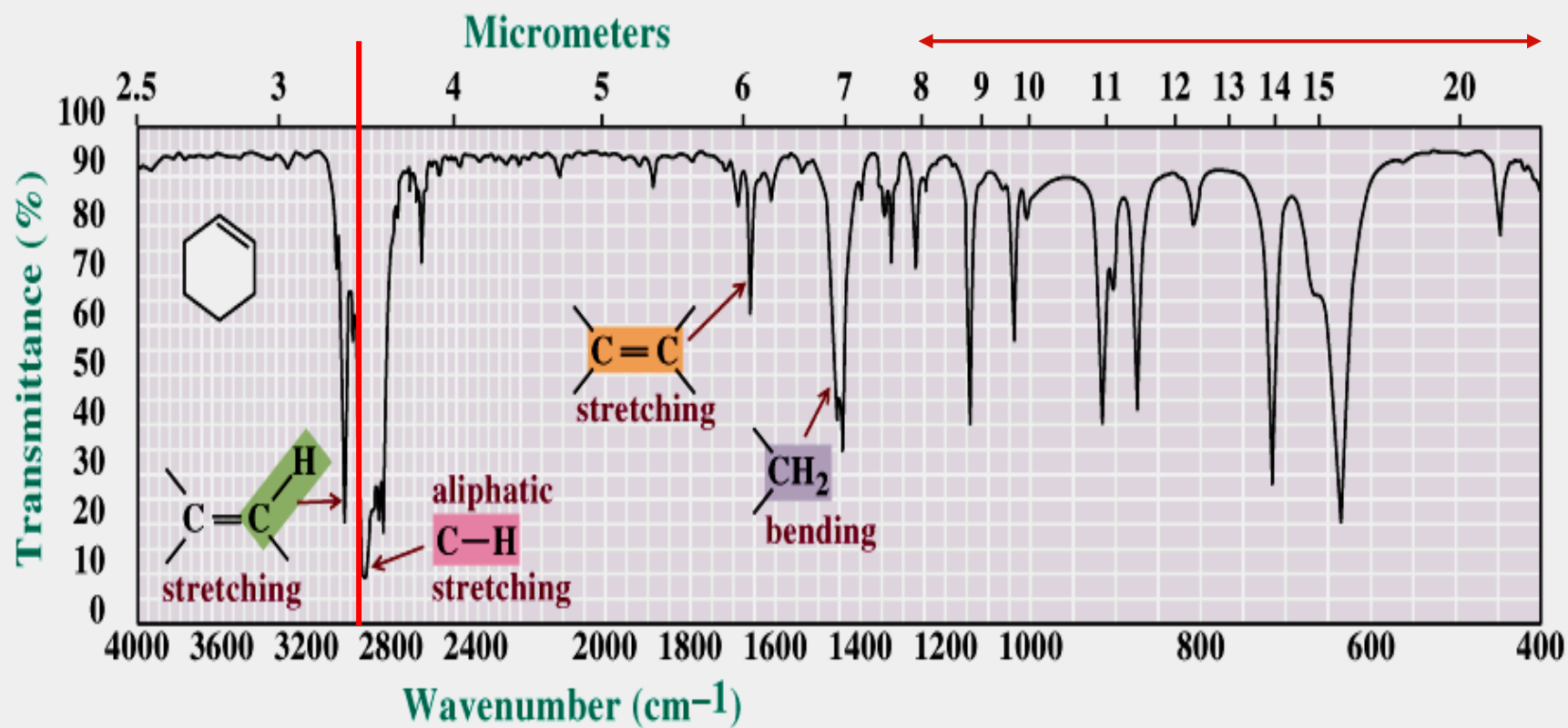


IR spectrum of decane

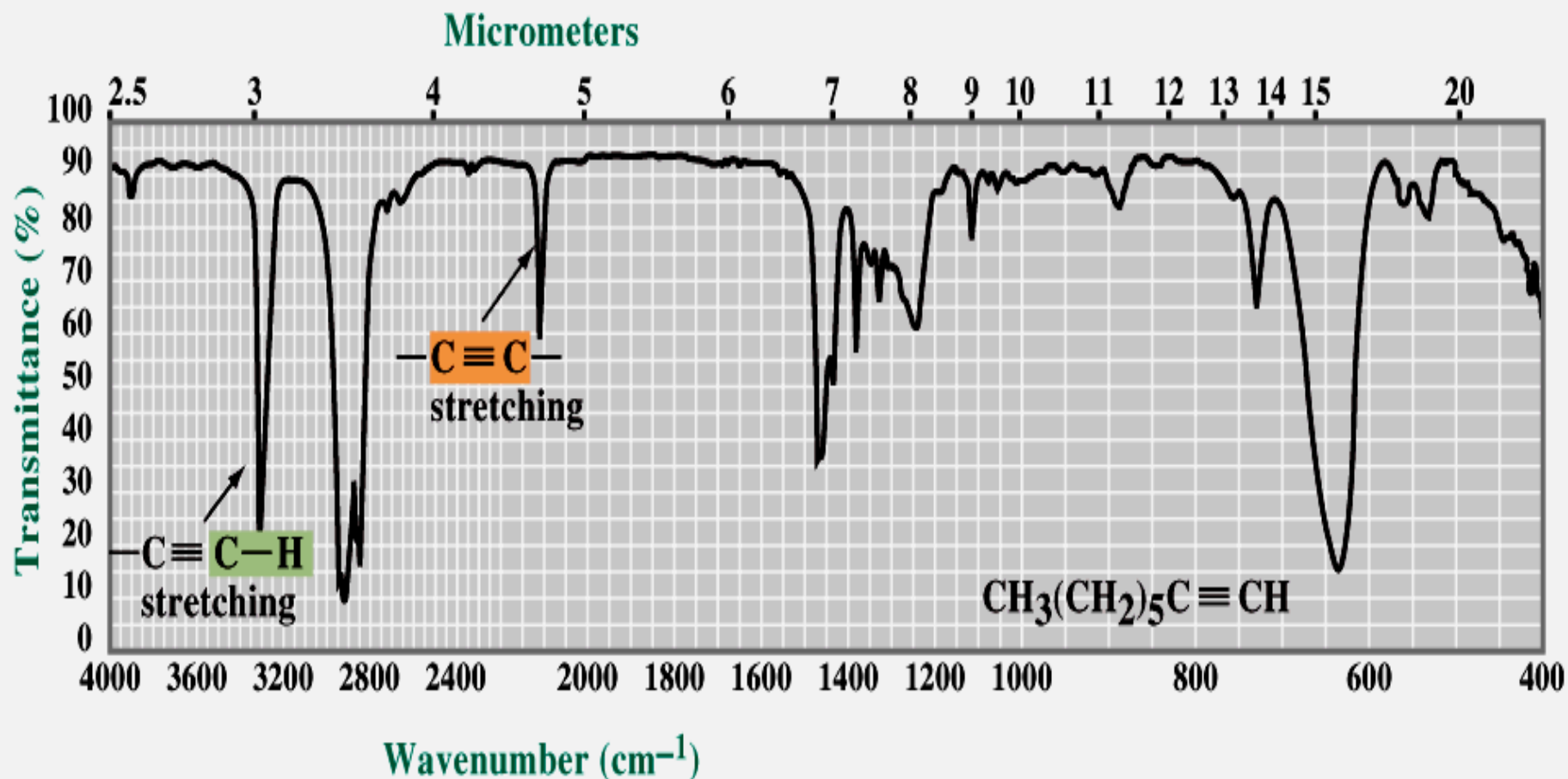


IR spectrum of cyclohexene

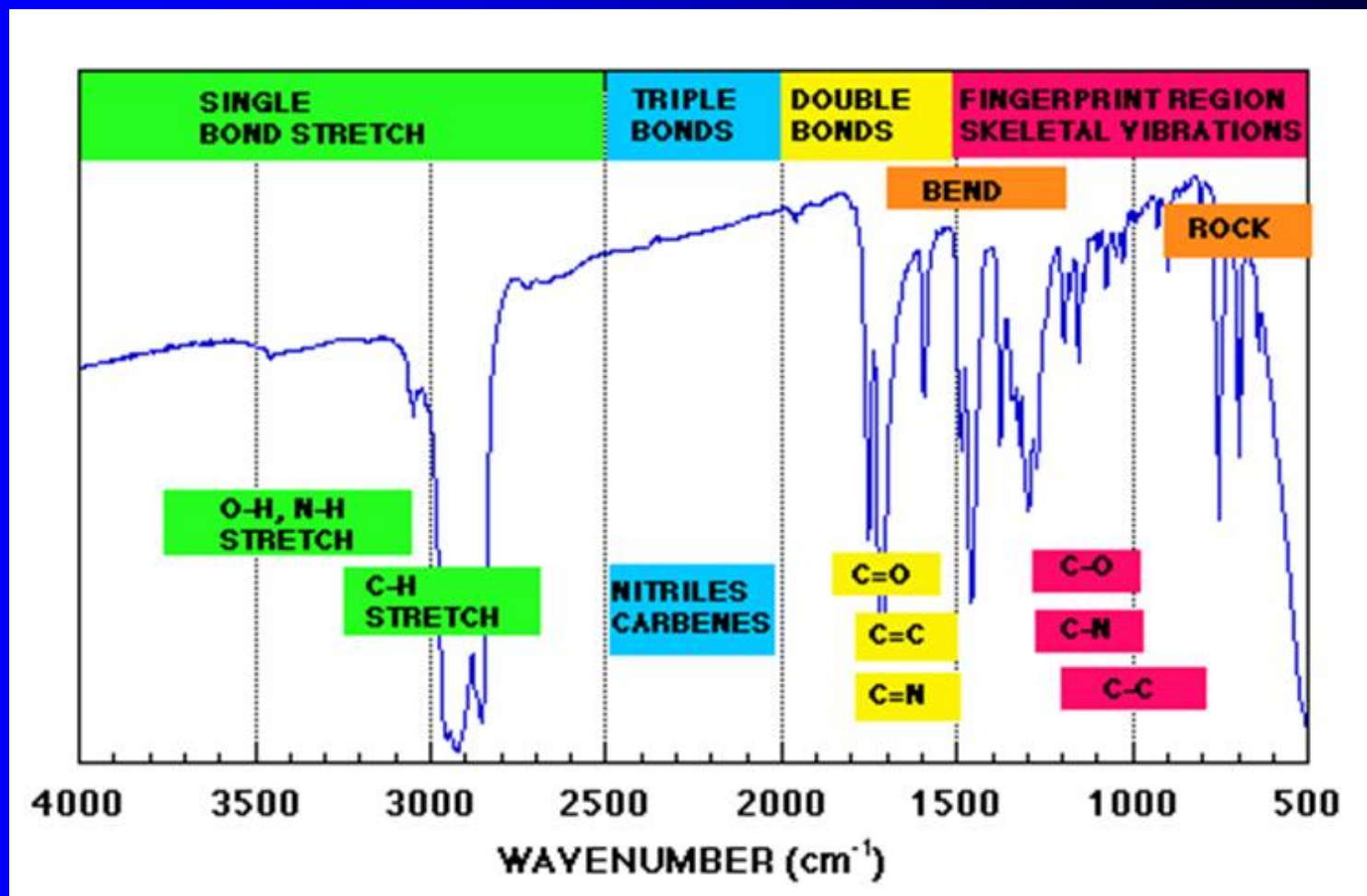
Fingerprint region



Infrared spectrum of 1-octyne



Infrared spectroscopy



Summary

- IR measures vibrational transitions
- Can be described by classical oscillator theory
 - Frequency proportional to $[\text{bond strength/mass}]^{1/2}$
- Characteristic Group Frequencies
 - OH and C=O are particularly easy to identify
- Know how to read the chart... cm^{-1} ??
- Practice at the online sites...nmr, IR..Excellent!!



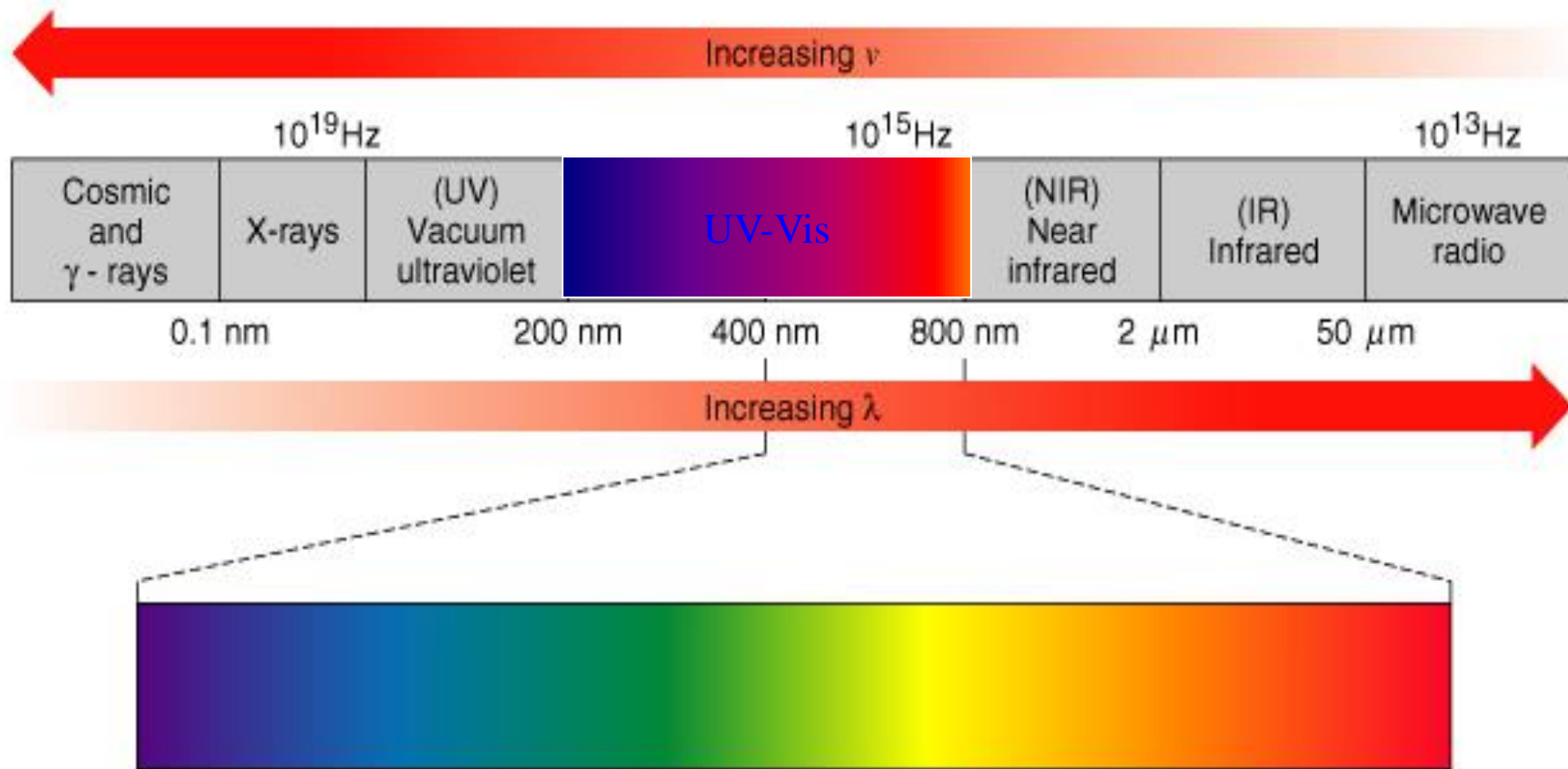
UV/Visible Spectroscopy

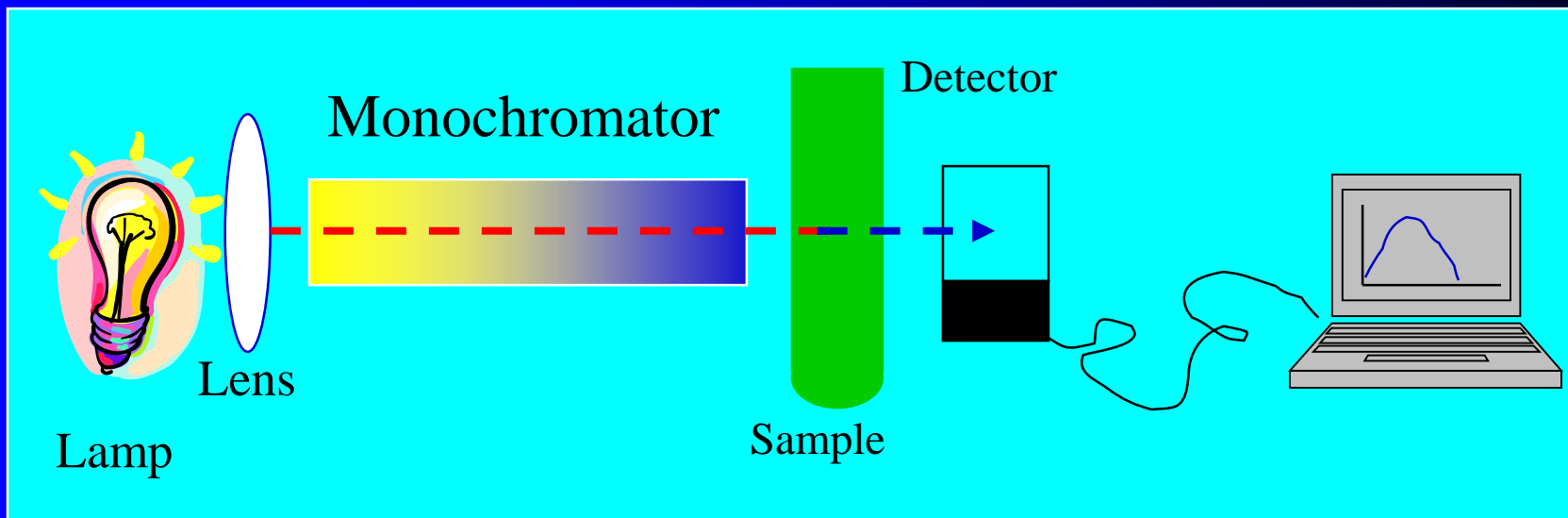
$$\text{Absorbance (A)} = \log \frac{I_0}{I}$$

$$\% \text{Transmission (T)} = \left[\frac{I}{I_0} \right] \times 100$$

$$\text{Beer-Lambert Law: } A = \epsilon c l$$







UV/Visible Spectroscopy

- Most UV/visible spectrophotometers cover from
 - 200 to 400 nm (the near ultraviolet) and
 - 400 nm (violet light) to 700 nm (red light)

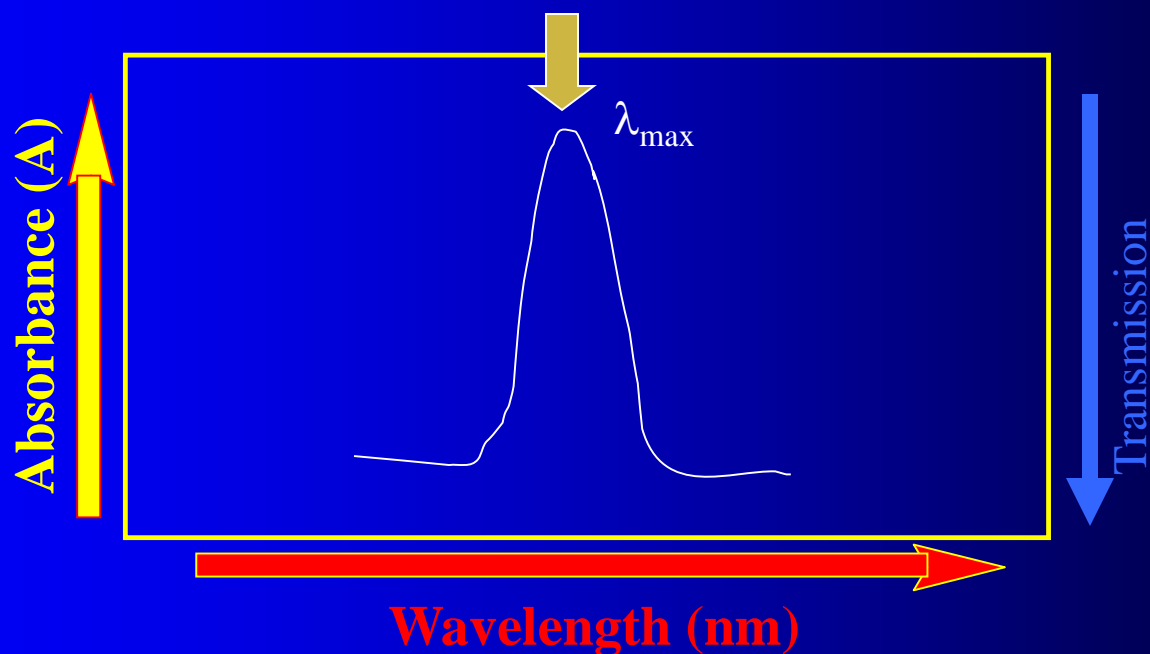
Region of Spectrum	Wavelength (nm)	Energy (kcal/mol)
ultraviolet	200-400	71.5 - 143
visible	400-700	40.9 - 71.5

C-C bond Disassociation energy ~ 95Kcal/mol

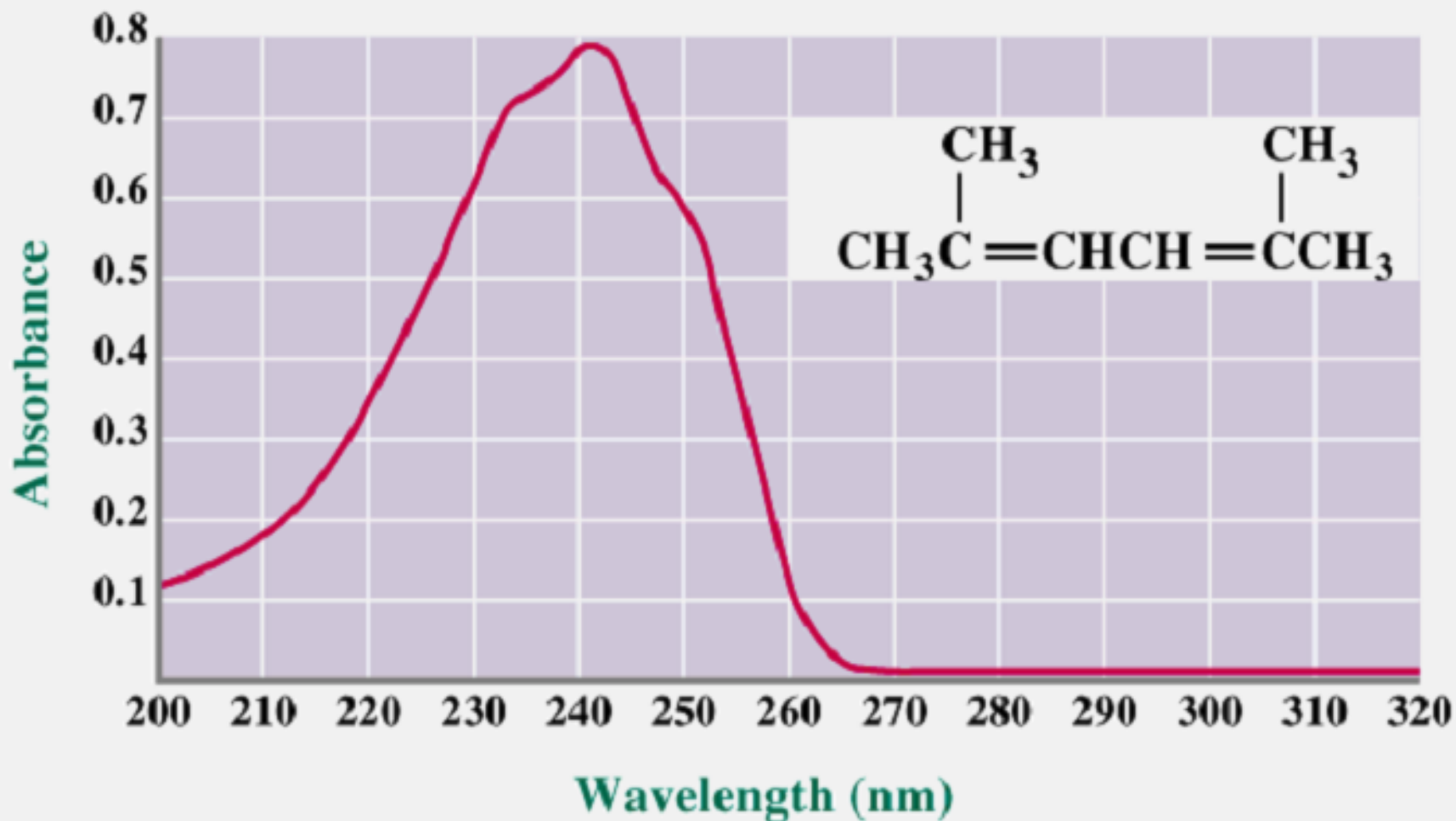


UV/Vis Spectroscopy

- UV-Vis spectral data are plotted as absorbance (A) versus wavelength (nm)



UV spectrum of 2,5-dimethyl-2,4-hexadiene



UV/Vis Spectroscopy

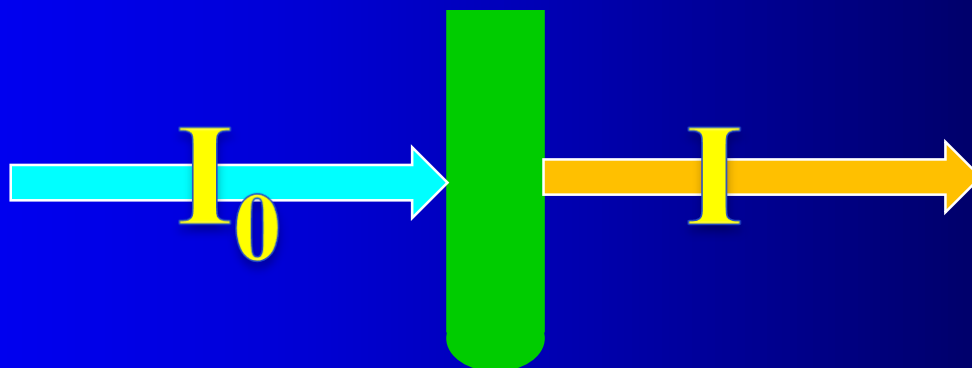
- **Absorbance:** a quantitative measure of the extent to which a compound absorbs ultraviolet-visible radiation at a particular wavelength

$$\text{Absorbance (A)} = \log \frac{I_0}{I}$$

Where:

I_0 is the intensity of the incident radiation on the sample

I is the intensity transmitted through the sample



UV/Vis Spectroscopy

- **Transmission:** a quantitative measure of the extent to which a compound absorbs ultraviolet-visible radiation at a particular wavelength

$$\% \text{Transmission (T)} = \left[\frac{I}{I_0} \right] \times 100$$

Where:

I_0 is the intensity of the incident radiation on the sample

I is the intensity transmitted through the sample



Beer-Lambert law

- **Beer-Lambert law:** the relationship between absorbance, concentration, and length of the sample tube

$$\text{Beer-Lambert Law: } A = \epsilon c l$$

A = absorbance

c = concentration ($\text{mol} \cdot \text{liter}^{-1}$)

l = length of the sample tube (cm)

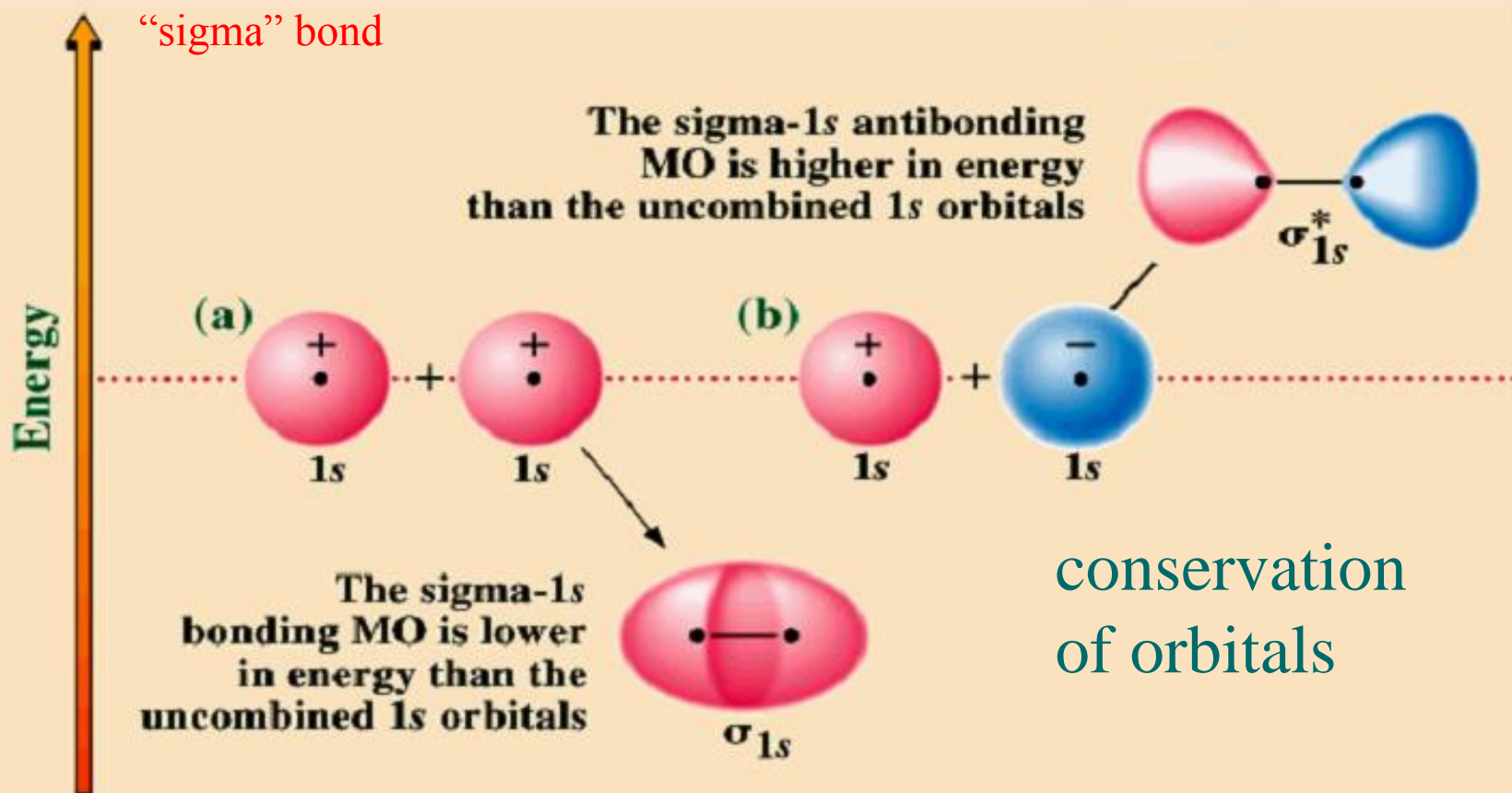
ϵ = molar absorptivity ($\text{liter} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$).

Experimental values of ϵ range from 0 to 10^6



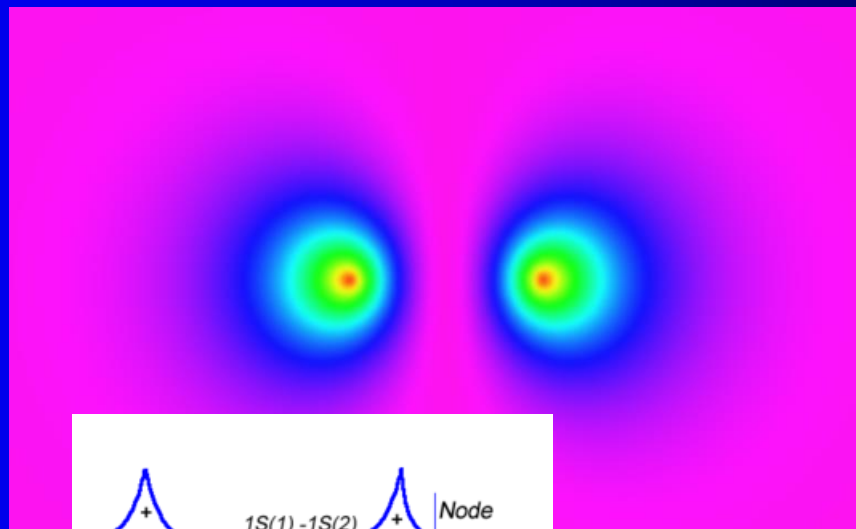
Origin of UV-Vis Absorbance - MO Theory

MOs derived from combination of two 1s atomic orbitals

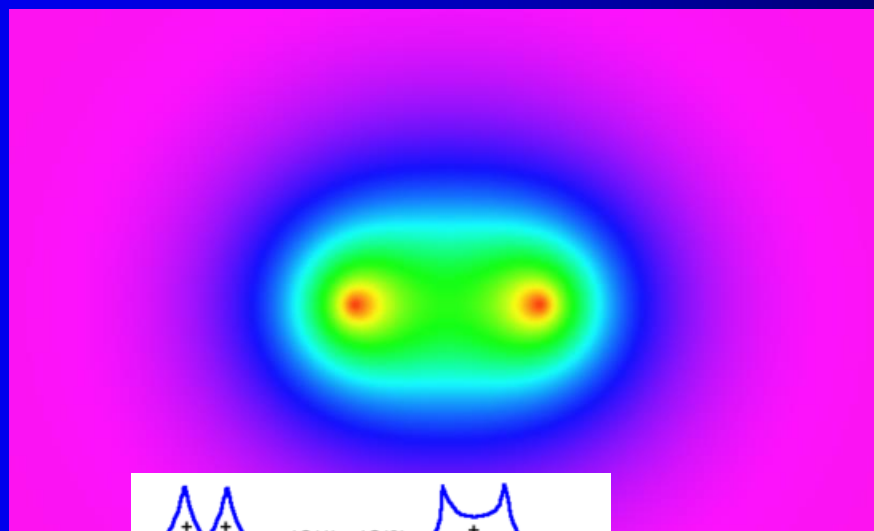
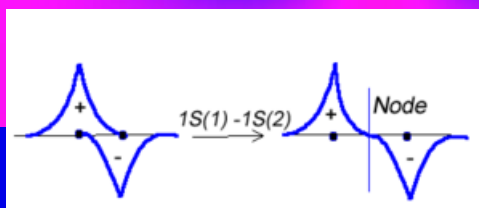


$$\Delta E = 65 \text{ Kcal/mole}$$

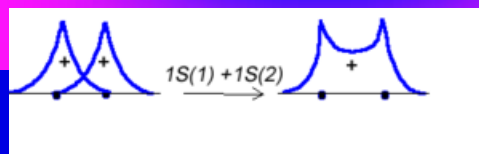


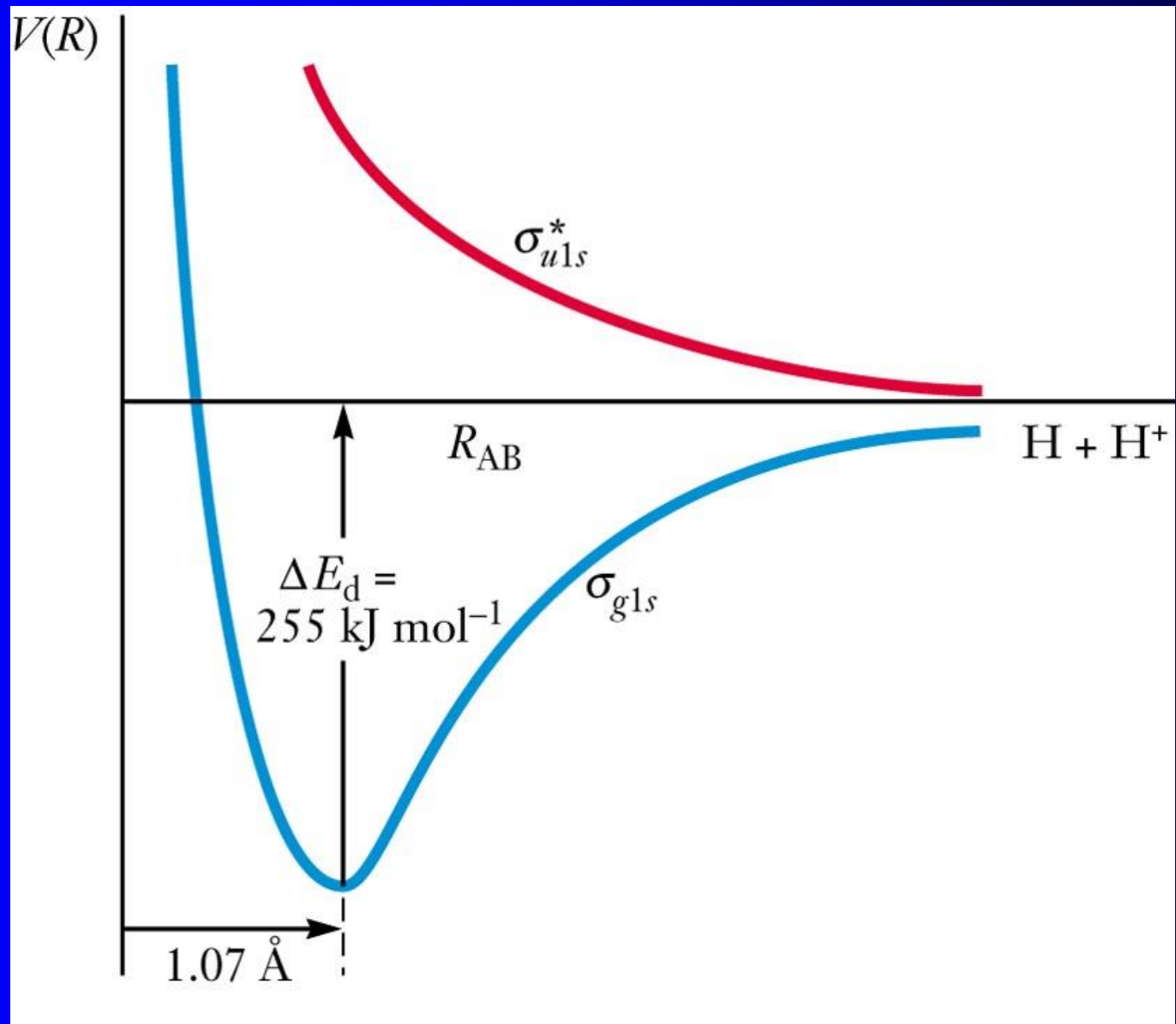


Antibonding



Bonding





Origin of UV-Vis Absorbance MO Theory

MO energy diagram for the hydrogen molecule, H₂

