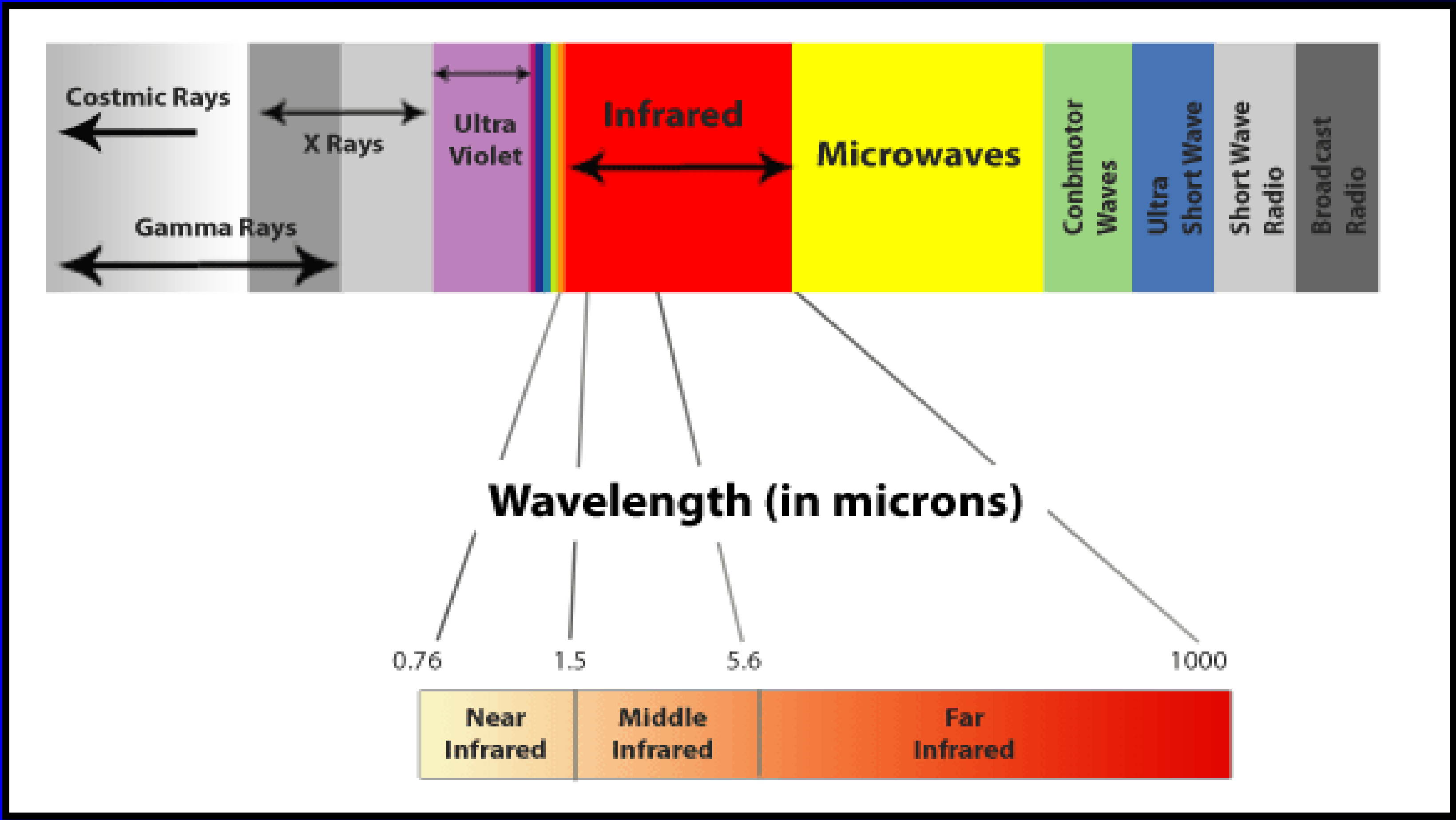
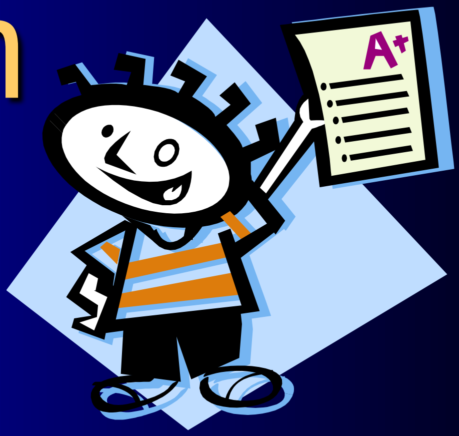
Lecture 7
Infrared spectroscopy



First Midterm Exam



- When: Wednesday, **2/20**
- When: 7-9 PM (please do not be late)
- Where: Painter 3.02!!!
- What: Covers material through Thursday's lecture
- Remember: Homework problems!!
- Practice: Old exams are posted on the web site
- Please…bring pencils, an eraser and a calculator only and no phones …….**<u>Do a good job!!!</u>**

I will bother you! ☺

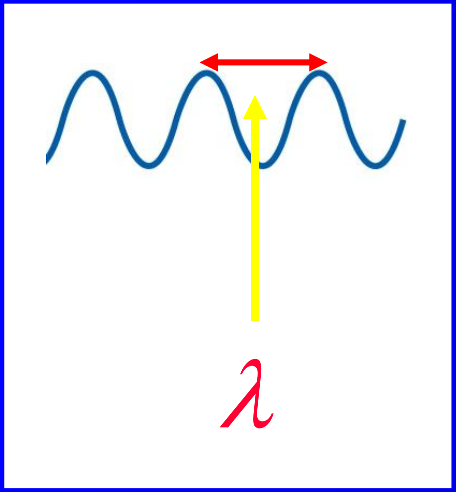
Early Exam Announcement

- Early Exam on 2/20 @ 5- 7PM in FNT 1.104
- Prior approval is required to take the exam early
- Note that the doors to FNT lock automatically at 5PM You MUST be on time and need to stay for the duration of the exam. You may not exit the exam room before 7 PM
- No Office Hours will be held on the day after the mid-term exams. (@/21, 3/28, 4/25

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 radiation



$$c = \lambda \upsilon \qquad \bar{\upsilon} = \frac{1}{\lambda}$$

$\bar{\upsilon}$
- (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)

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

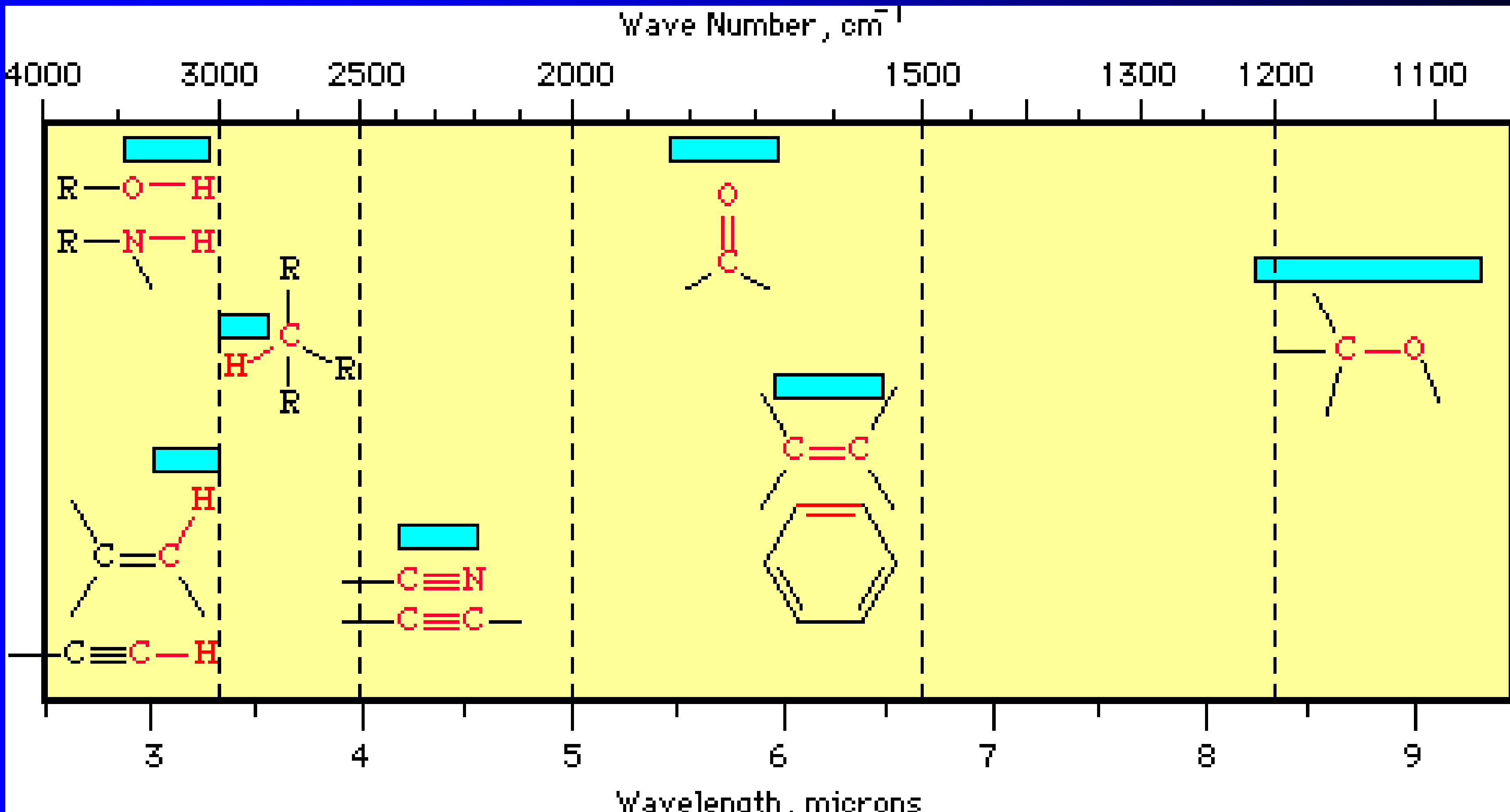
10 microns (micrometers) = 1000 cm^{-1}

Infrared Absorption Frequencies

Stretching vibrations (multiple bonds)

Structral unit	Frequency, cm^{-1}
$>C=C<$	1620-1680
$-C\equiv C-$	2100-2200
$-C\equiv N$	2240-2280

IR Group Correlation Tables



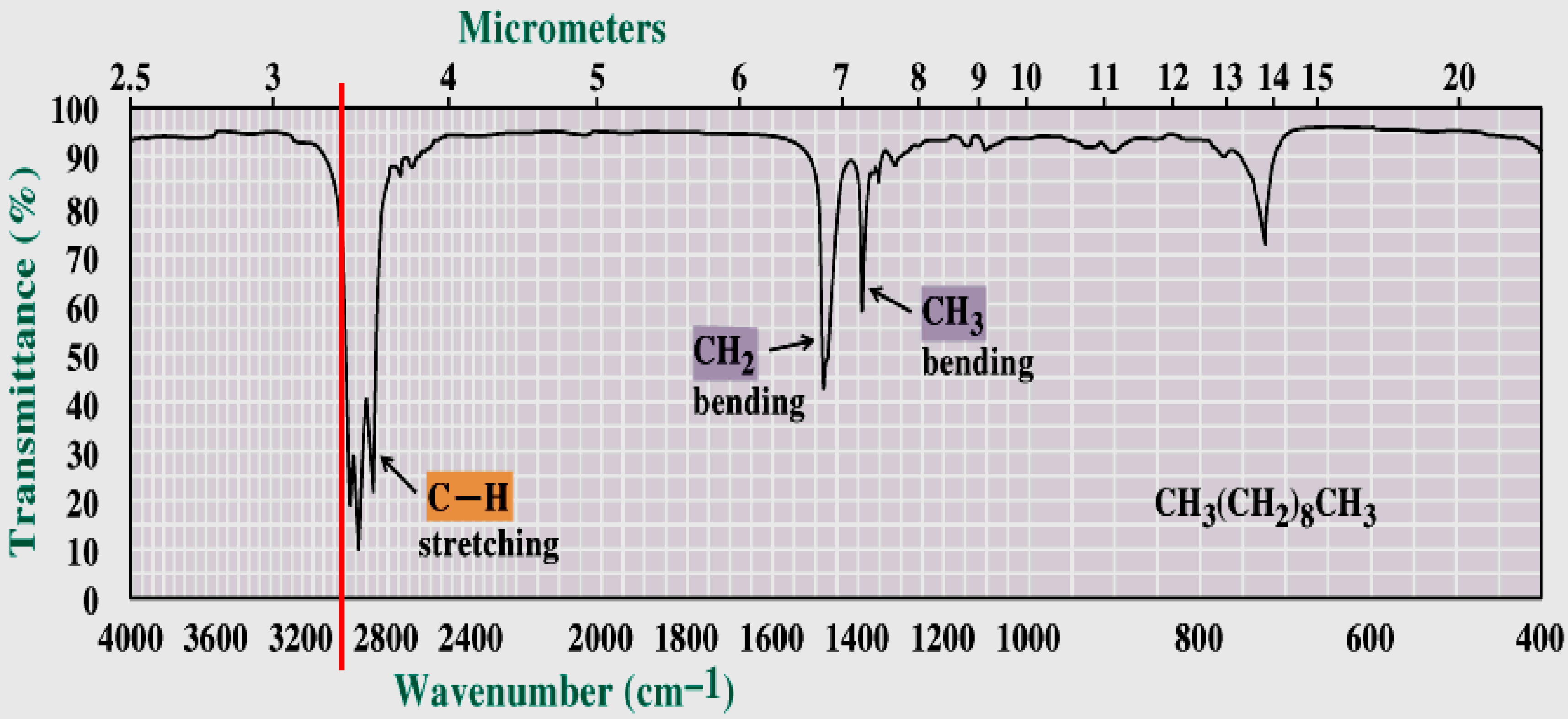
IR Group Correlation Tables

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

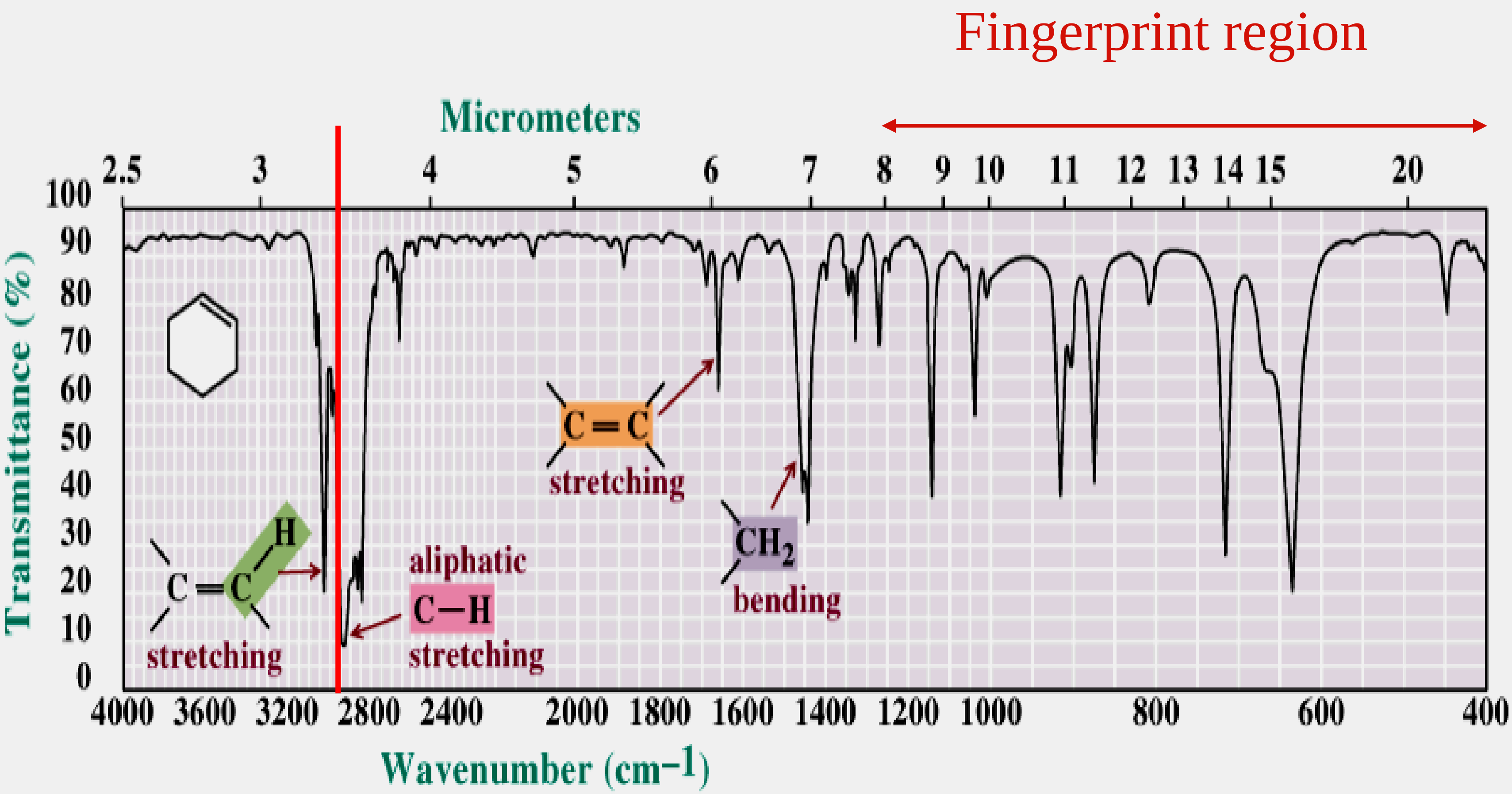
Bond	Frequency (cm^{-1})	Intensity
O-H	3200-3650	strong and broad
N-H	3100-3500	medium
C-H	2850-3300	medium to strong
C=O	1630-1810	strong
C=C	1600-1680	weak
C-O	1050-1250	strong

Hydrocarbon	Vibration	Frequency (cm^{-1})	Intensity
Alkane			
C-H	stretching	2850 - 3000	strong
CH_2	bending	1450	medium
CH_3	bending	1375 and 1450	weak to medium
Alkene			
C-H	stretching	3000 - 3100	weak to medium
C=C	stretching	1600 - 1680	weak to medium
Alkyne			
C-H	stretching	3300	medium to strong
C≡C	stretching	2100-2250	weak

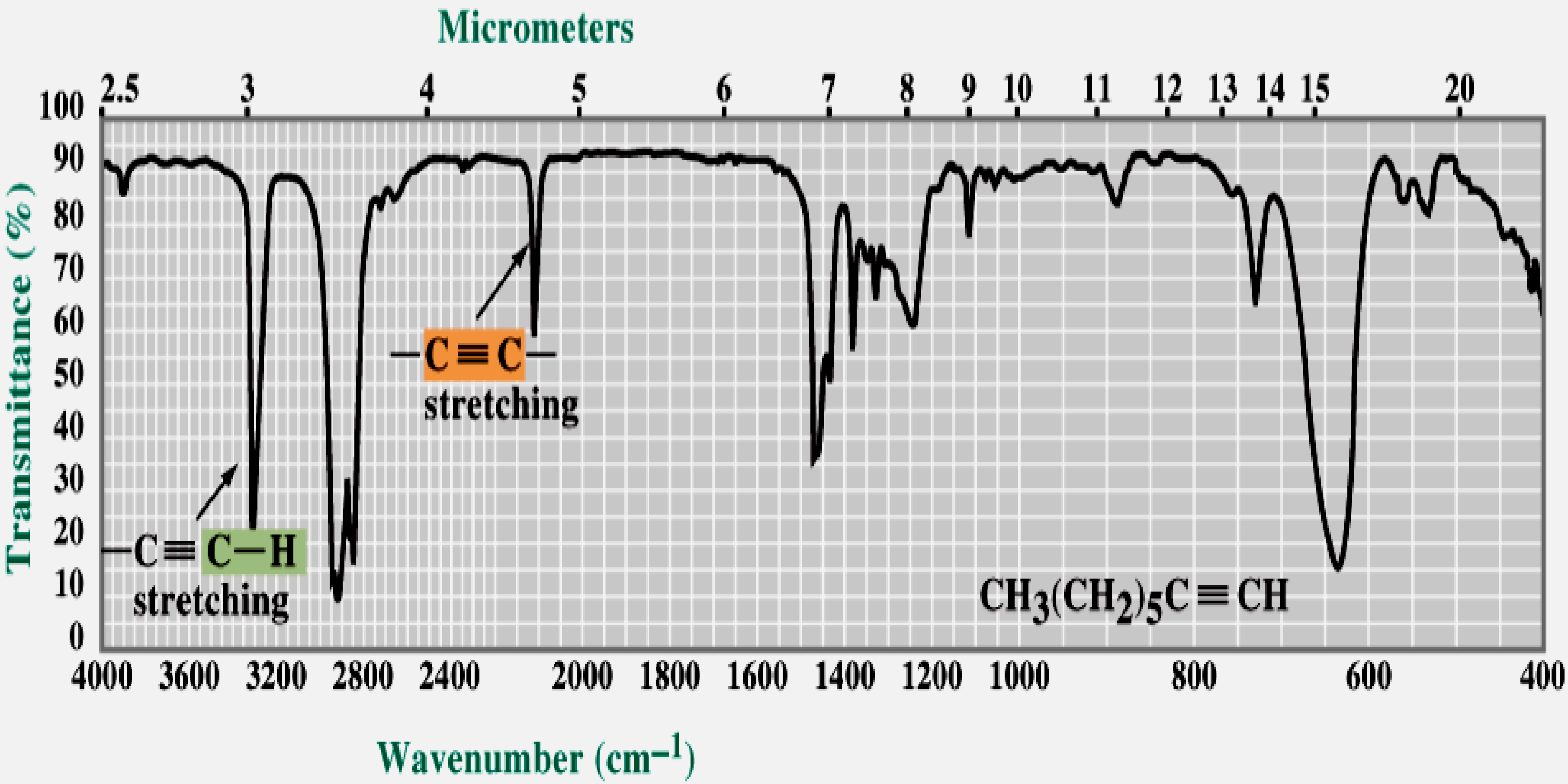
IR spectrum of decane



IR spectrum of cyclohexene

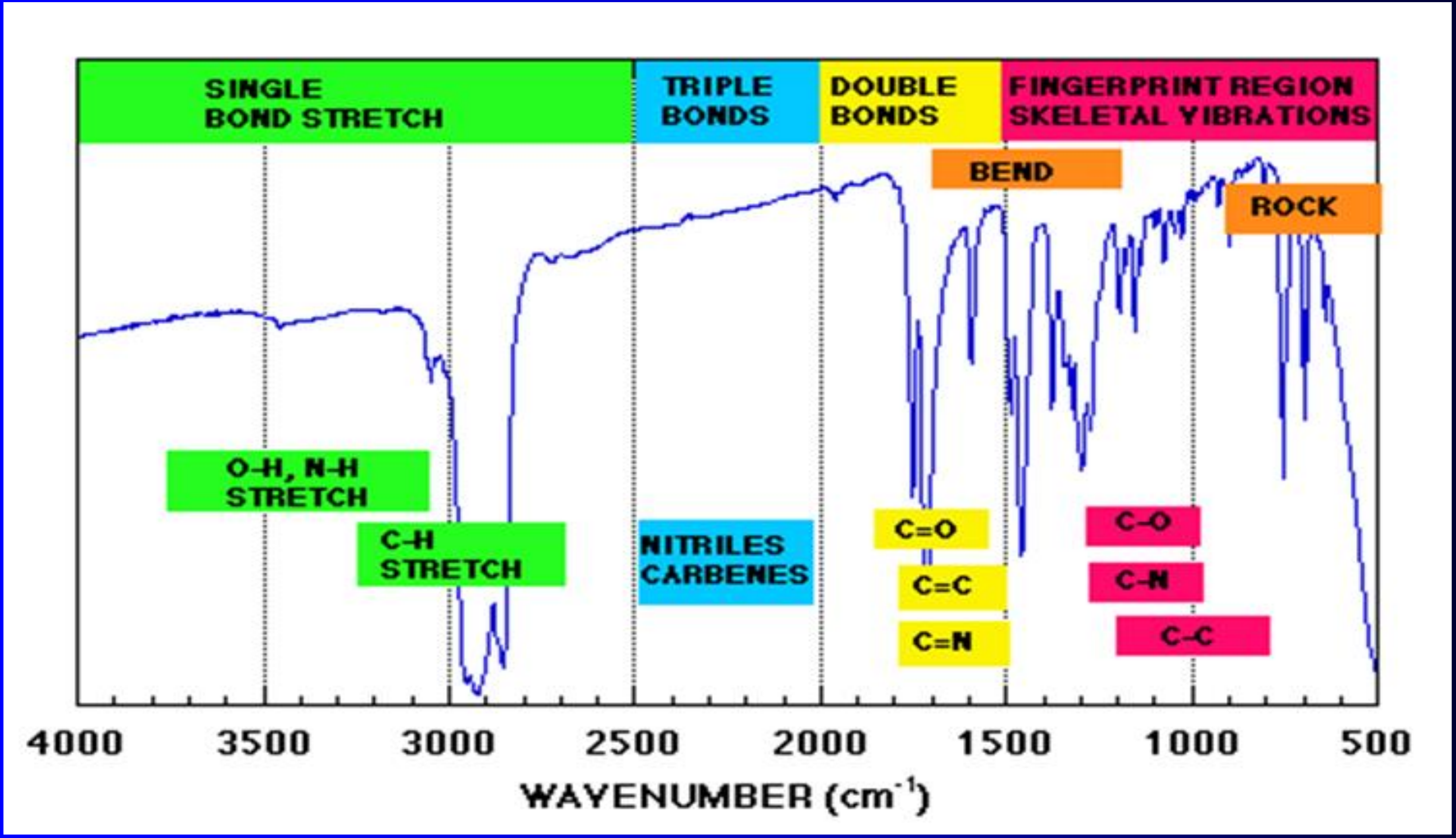


Infrared spectrum of 1-octyne



IR

Infrared spectroscopy



Summary

- IR measures vibrational transitions
- Can be described by classical oscillator theory
  - Frequency proportional to [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!!

Organic Structure Elucidation Workbook - Microsoft Internet Explorer provided by Dell

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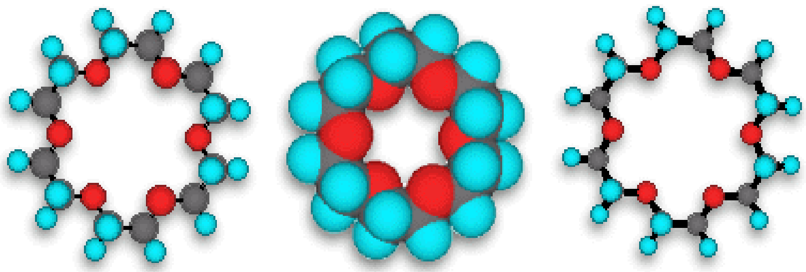
Organic Structure Elucidation

A Workbook of Unknowns



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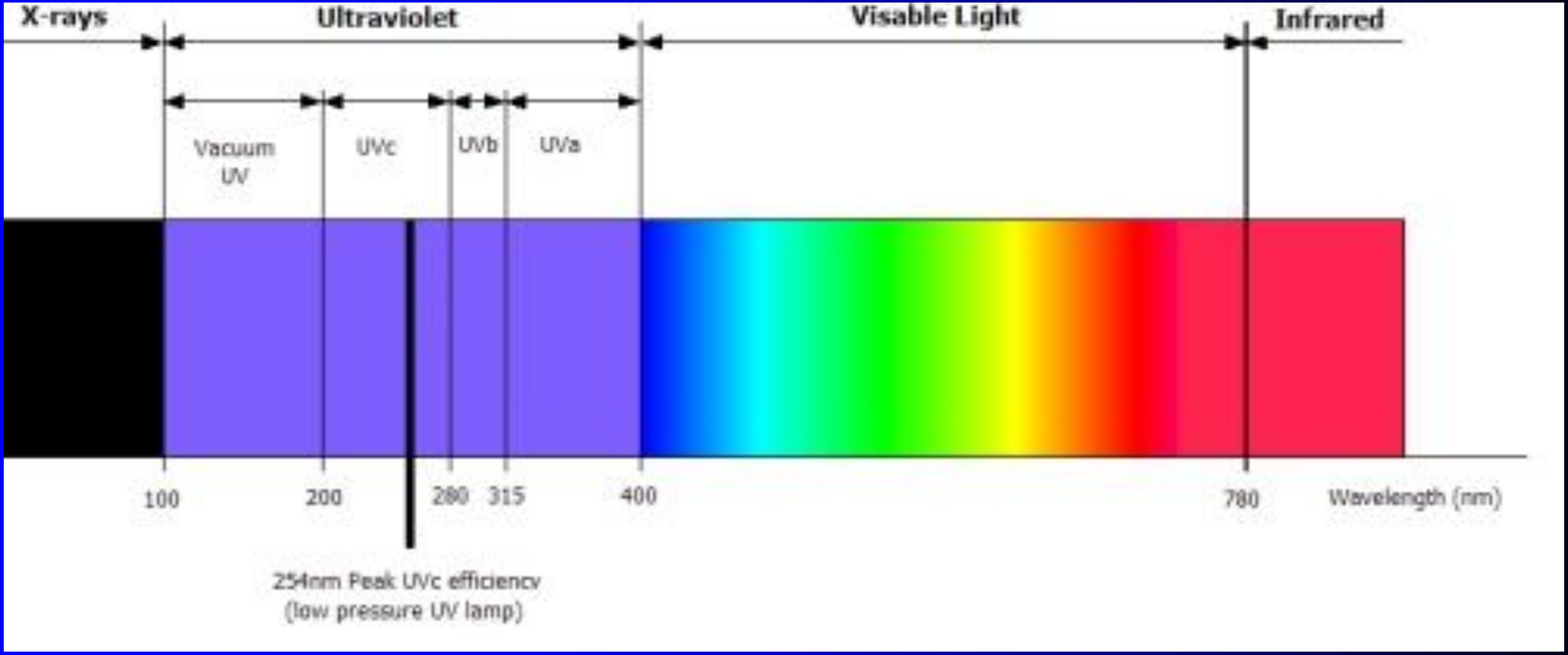
Done Internet

Practice Problems & Tutorials

- https://nb.khanacademy.org/science/organic-chemistry/spectroscopy-jay/infrared-spectroscopy-theory/v/ir-spectra-practice
- https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/questions/Spectroscopy/irmsprb/infrared.htm
- https://webspectra.chem.ucla.edu/
- https://chemistry.boisestate.edu/richardbanks/organic/mc/vol8/mcquestions317h.htm
- https://www.masterorganicchemistry.com/2016/11/29/ir-spectroscopy-some-simple-practice-problems/
- https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/spectrpy/infrared/infrared.htm

UV-visible Spectroscopy



UV/Visible Spectroscopy

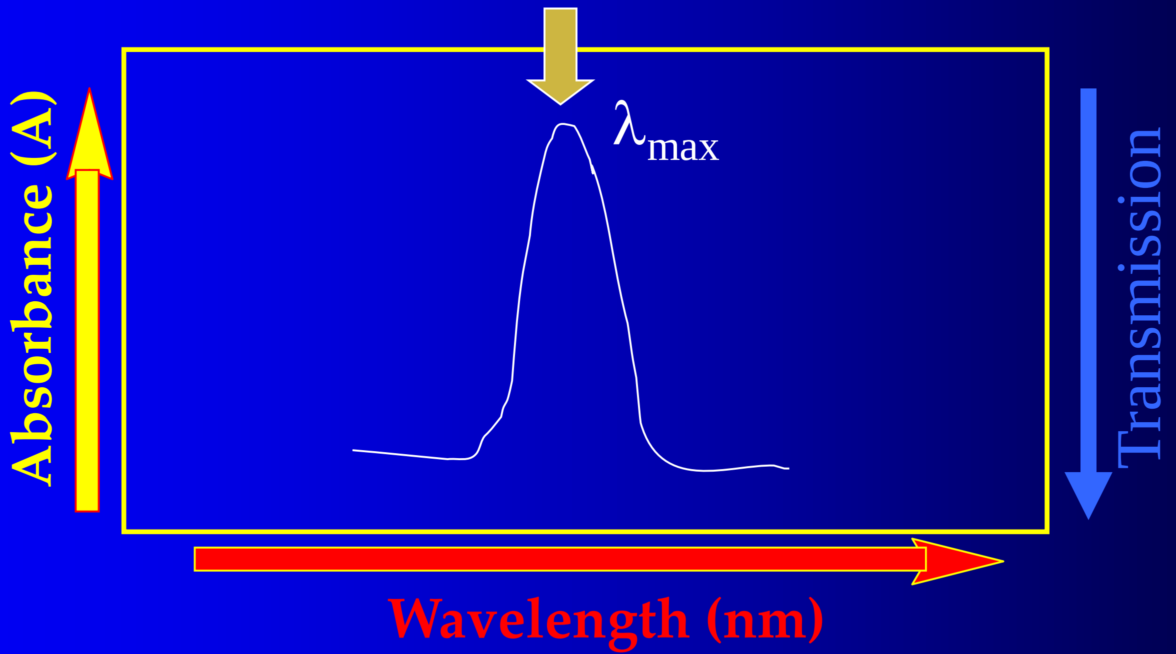
- Most UV/visible spectrophotometers cover from
  - 200 to 400 nm (the near ultraviolet) and
  - 400 nm (violet light) to 700 nm (red light)

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

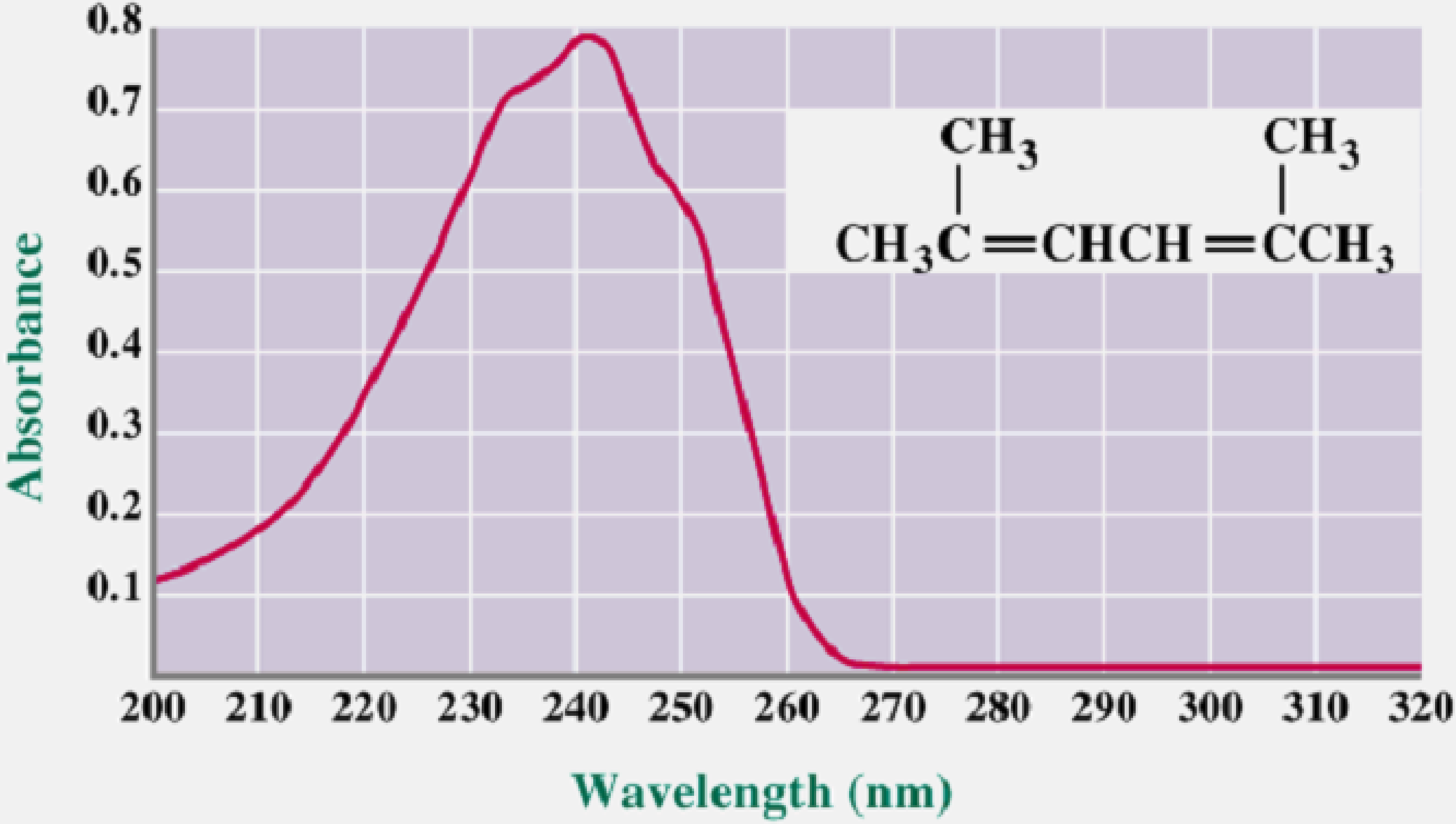
C-C bond Disassociation energy ~ 95Kcal/mol

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

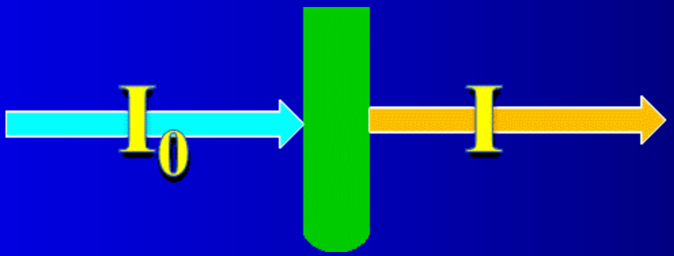
Transmission: a quantitative measure of the extent to which a compound absorbs ultraviolet-visible radiation at a particular wavelength

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

Where:

I_0 is the intensity radiation incident on the sample

I is the intensity transmitted through the sample



UV/Vis Spectroscopy

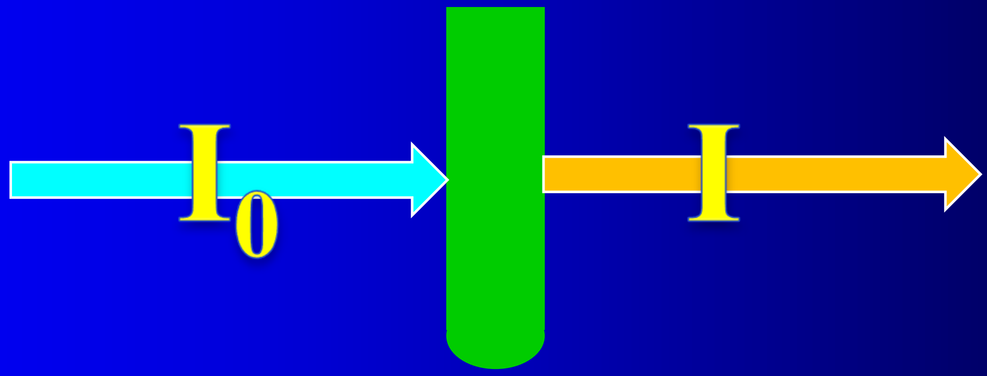
- **Absorbance:** a quantitative measure of the extent to which a compound absorbs ultraviolet-visible radiation at a particular wavelength

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

Where:

I_0 is the intensity radiation incident 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

Beer-Lambert Law: $A = \varepsilon c l$

A = absorbance

c = concentration (mol • liter^{-1})

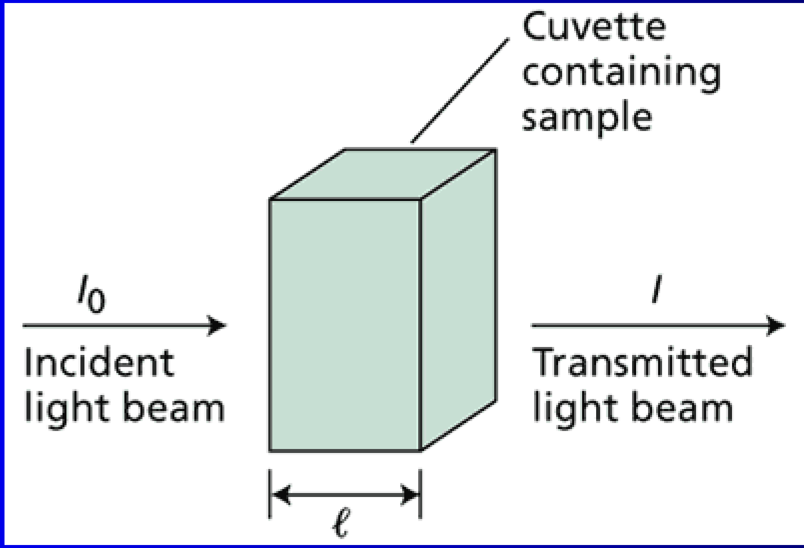
l = length of the sample tube (cm)

ε = molar absorptivity (liter • mol^{-1} • cm^{-1}).

Experimental values of ε range from 0 to 10^6

Some Quantitative Relationships

Please read: Pages 904-908

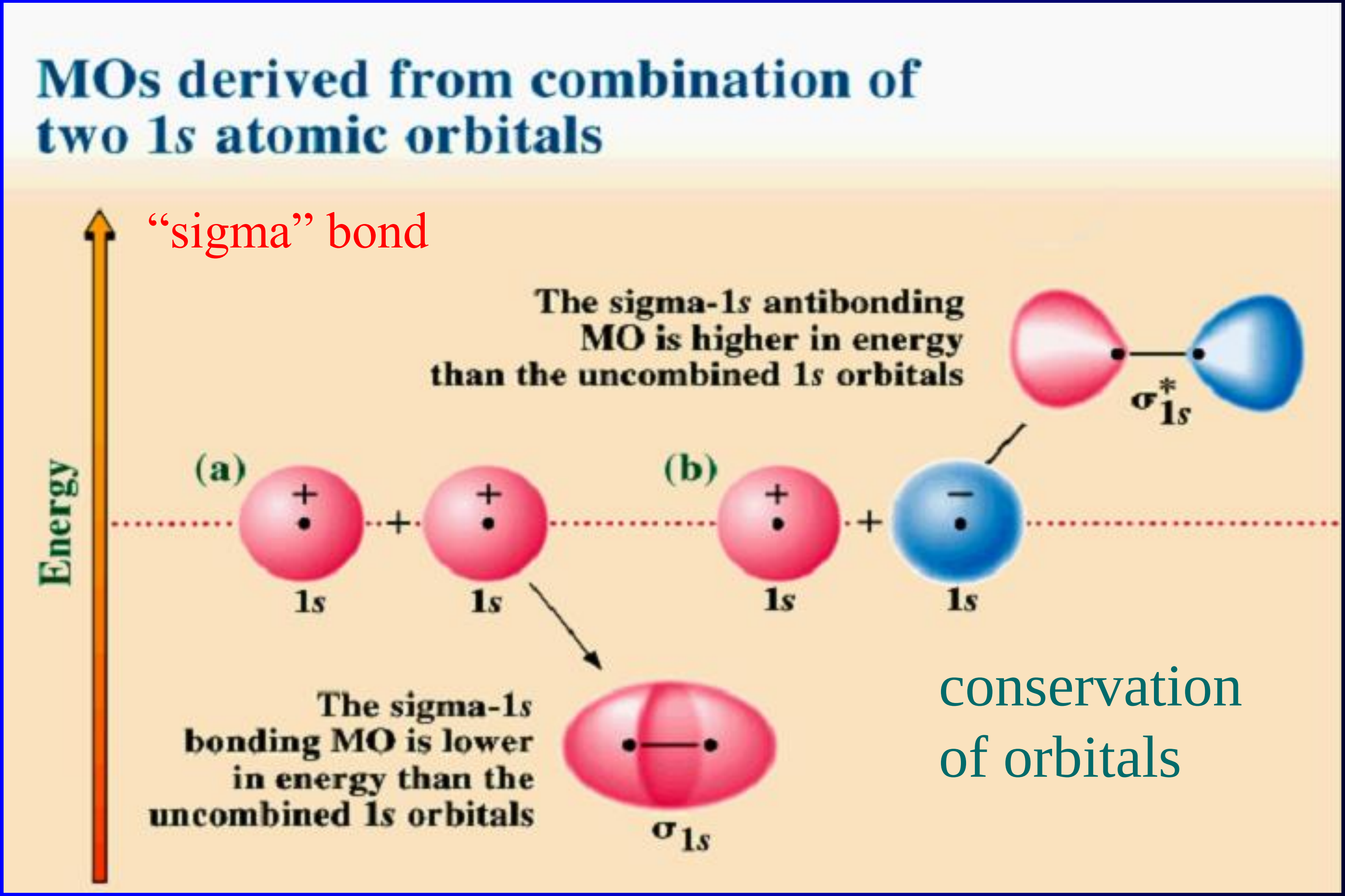


$$\%\text{Transmission (T)} = \left(\frac{I}{I_o}\right) \times 100$$

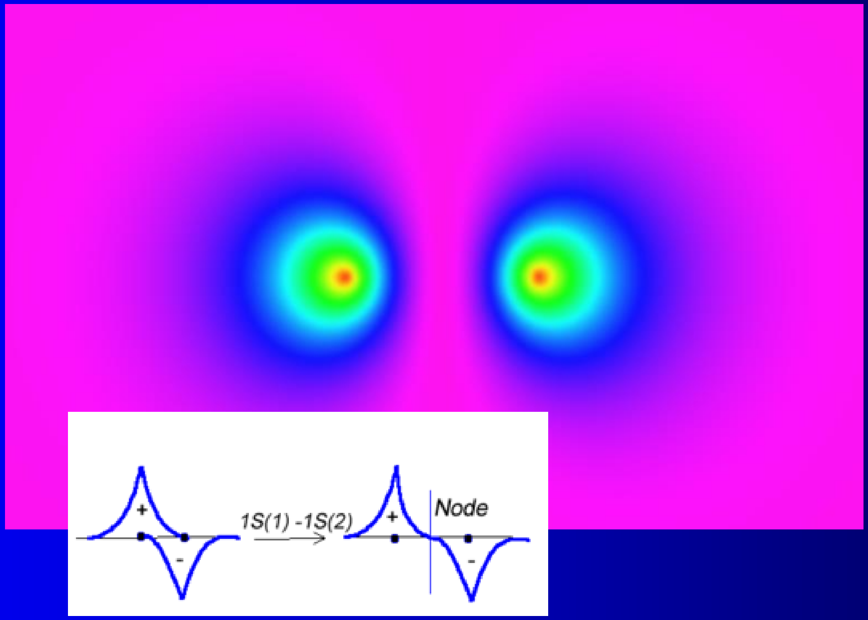
$$\text{Absorbance (A)} = \log \frac{I_o}{I}$$

Beer-Lambert Law: A = ε c l

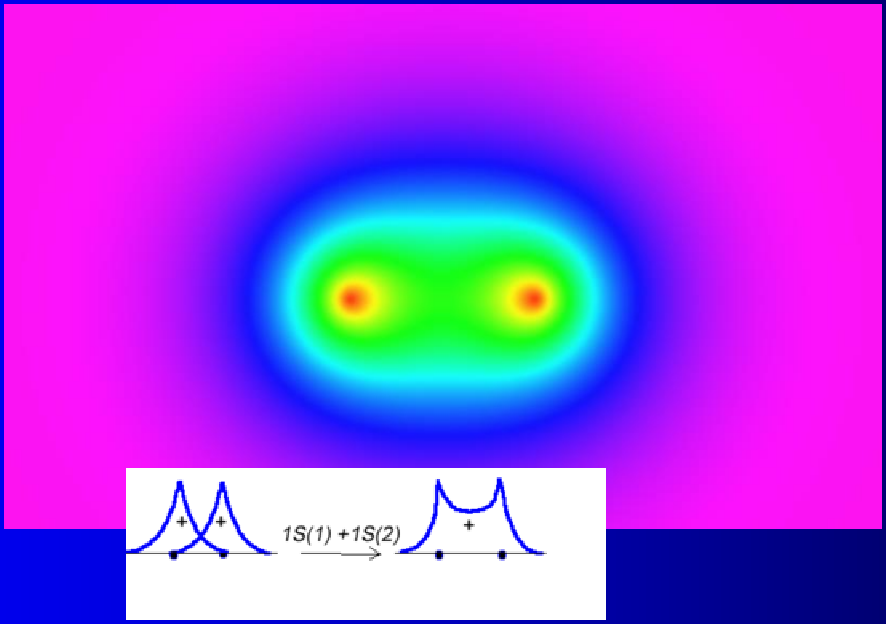
Origin of UV-Vis Absorbance - MO Theory



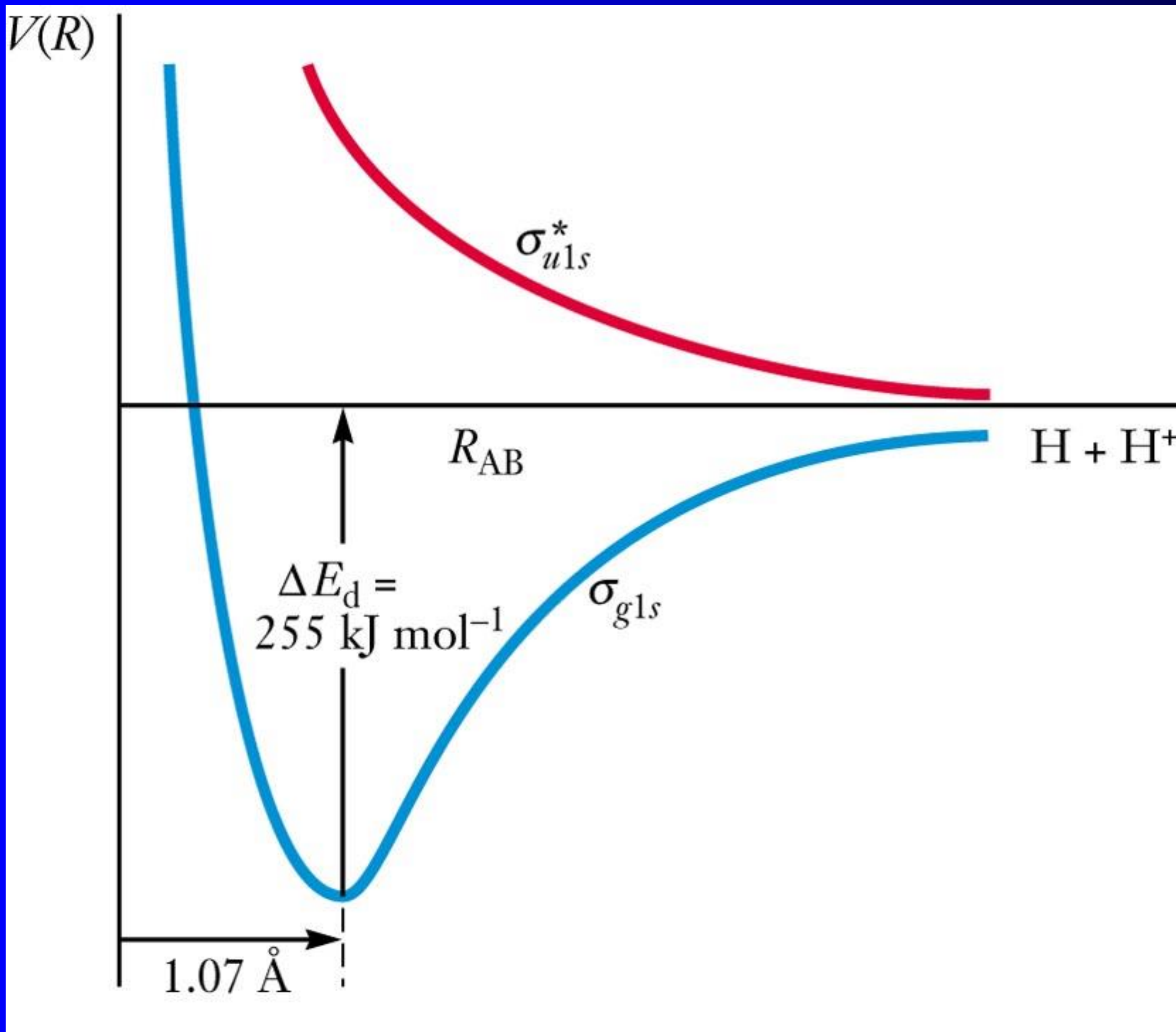
$\Delta E = 65$ Kcal/mole



Antibonding



Bonding


V(R)
σ*u1s
RAB
H + H+
ΔEd =
255 kJ mol−1
σg1s
1.07 Å