CHEM 222 section 01

LECTURE #07 Tues., Sept.25, 2007

Lecture topics & readings

Today's class

- UV/Vis spectroscopy (sections 12.16-12.20)

Before next class

- read section on IR spectroscopy in Bruice
- read Lehman's Operation section on IR

Next class

- IR spectroscopy (sections 12.6-12.15)

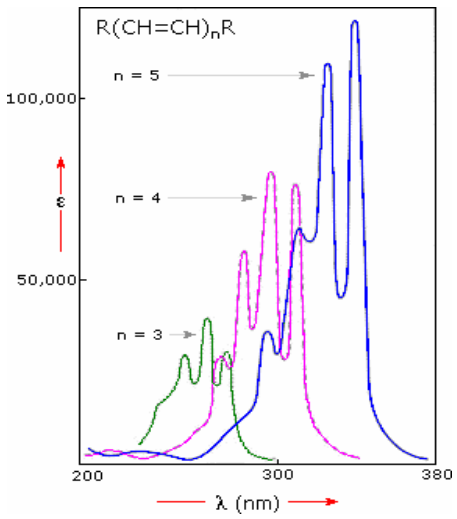
(1) **Helpful website for spectroscopy topics: Michigan State University**
http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/spectro.htm#contnt

FYI: Terminology used to describe shifts in spectra

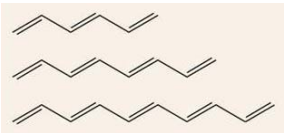
Shift to…		Term used
Longer wavelength	= lower energy transitions	bathochromic
Shorter wavelength	= higher energy transitions	hypsochromic
Greater absorbance	= transition probability ↑	hyperchromic
Lower absorbance	= transition probability ↓	hypochromic

(2) **From:**
http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/UV-Vis/spectrum.htm

Effects of conjugation (extended π-systems)



n=3
n=4
n=5



As conjugation length ↑

⇩

orbital E gaps ↓

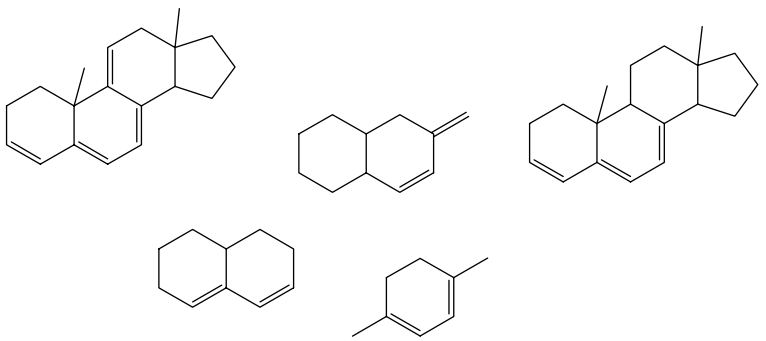
⇩

absorbance λ_{max} ↑

General trends:	
Difference…	…λ_{max} ↑ by
+ 1 conj. C=C	30-40 nm
+ 1 alkyl group	5 nm

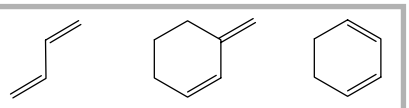
(3) Image from:
http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/UV-Vis/spectrum.htm

Match the diene with its λ_{max}: 232, 237, 273, 313, 353 nm



Reference values:

λ_{max}



217 nm 232 nm 256 nm

(4)

Trends in UV/Vis spectra: Typical λ_{max} of functional groups

Data from: http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/UV-Vis/spectrum.htm

Chromophore	Example	Excitation	λ_{max} (nm)	ε ($M^{-1}cm^{-1}$)	solvent
C=C	ethene	**π-π^***	**171**	**15,000**	hexane
C≡C	1-hexyne	π-π^*	180	10,000	hexane
C=O	ethanal	**n-π^***	**290**	**15**	hexane
		π-π^*	**180**	**10,000**	hexane
N=O	nitromethane	n-π^*	275	17	ethanol
		π-π^*	200	5,000	ethanol
C–X (X=Br)	methyl bromide	n-σ^*	205	200	hexane
(X=I)	methyl iodide	n-σ^*	255	360	hexane

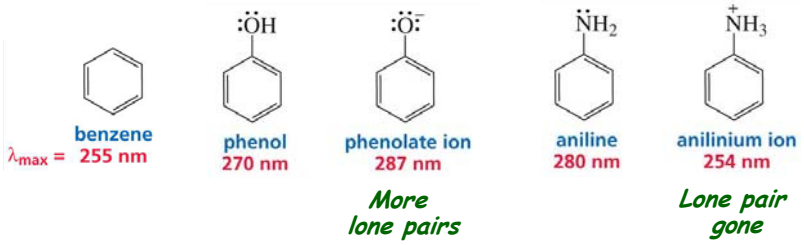
IMPORTANT: the shape of a chromophore's spectrum can vary

- Orbital Es influenced by environment ⇨ **λ_{max} & intensities can change**
  1. **Solvent polarity:** water → ethanol → hexane…
  2. **Substituents:** EDG *vs.* EWG connected to chromophore

Energies of orbitals are influenced by environment
∴ exact λ_{max}, peak intensities, spectral shape can change

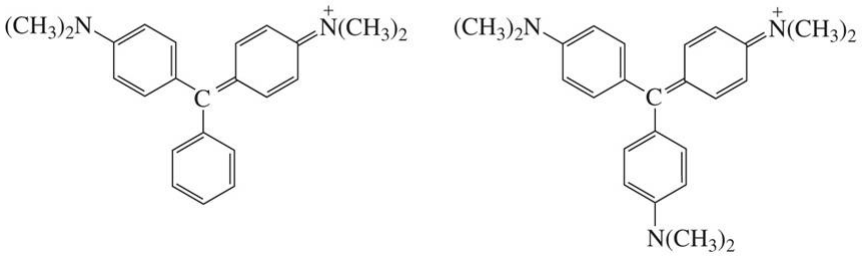
2. **Substituent effects**: "Auxochromes"
   = substituents that change absorbance λ_{max} and/or intensity

EDG conjugated to chromophore ⇨ *HOMO more e^--rich* ⇨ *Lower $\Delta E_{HOMO-LUMO}$* ⇨ *Larger λ_{max}*



Bruice problem 38: UV/Vis absorption & colour… and pH

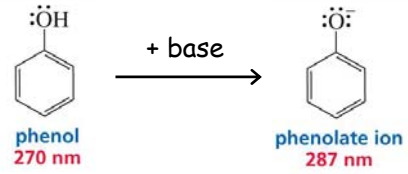
a. At pH = 7, one of the ions shown below is purple and the other is blue. Which is which?
b. What would be the difference in the colors of the compounds at pH = 3?

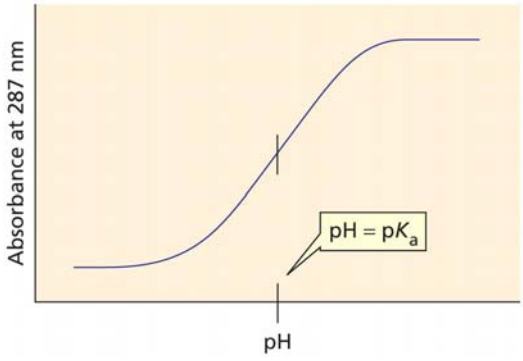


Applications of UV/Vis spectra: biology / biochemistry

1. **Determining pK_a:** if colour changes with pH

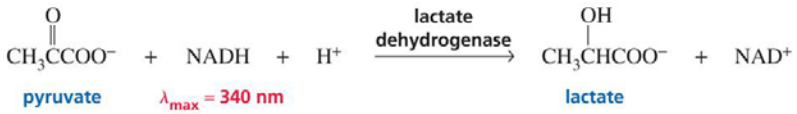
- Phenol = analog of amino acid *tyrosine*
- Amino acid pK_a is sensitive to environment
  - *e.g.,* can learn about protein's active site *etc…*



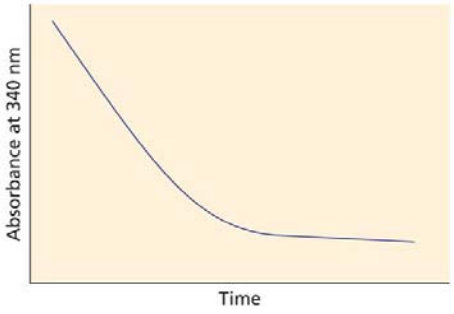


Applications of UV/Vis spectra: biology / biochemistry

2. **Studying reaction rates:** *e.g.,* in biological assays



- No other species in mixture absorbs at 340 nm…



3. **And many others…**