Chapter 26

Molecular Absorption Spectrometry

Molar Absorptivities

- Beer's Law: $A=\varepsilon bc$
- *What would be the maximum value of ε in theory?*

- $\varepsilon = 8.7 \times 10^{19} S \times P$ (0~10^5 L/(cm mol)
- S: cross section of molecule in cm^2 (~10^{-15} cm^2)
- P: Probability of the electronic transition (0-1)
  - P>0.1-1 → allowable transitions, strong absorption band, $\varepsilon_{max} = 10^4$~10^5
  - P<0.01 → forbidden transitions, $\varepsilon_{max} < 10^3$

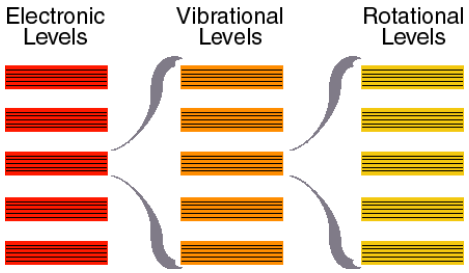
How Sensitive of the UV-Visible Spectrometry Would be?

- Assume A = 0.01 (with large instrumental error%), b = 1.00 cm, c = ? M
- $c = A/(\varepsilon_{max} b) = 0.01/(10^5 \times 1) = 1 \times 10^{-7}$ M

$$c_{min} = 10^{-6}\text{-}10^{-7} \text{ M}$$

Molecular Absorptions

$$E_{total} = E_{rotational} + E_{vibrational} + E_{electronic}$$



UV-VIS Spectroscopy

UV-Visible excitation→

Electronic Transitions in Molecules

--The absorption of the light source over wavelength → UV-Visible spectra

What is the electronic transition?

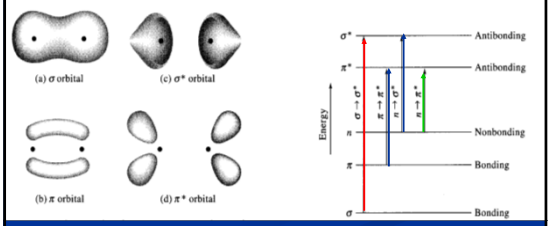
photon absorption promotes an electron from a bonding to an anti-bonding orbital

Molecular Absorption

- M + hν → M*
  (Absorption 10^{-8} sec)
- M* → M + heat
  (Most of Organic Molecules)
  (Thermal relaxation process)
- M* → A+B+C
  (Photochemical decomposition)

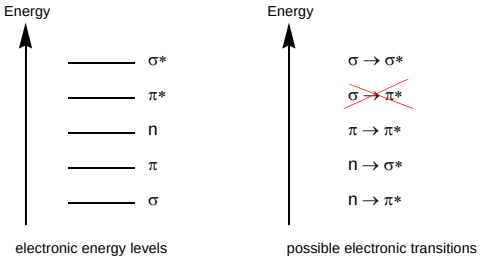
Molecular Transitions for UV-Visible Absorptions

- What electrons can we use for these transitions?



Energy Levels and Transitions

(4 Types)



σ → σ* Transition (Rarely Used for UV-Vis)

- Methane, λ_{max} = 125 nm, (C-H Bonds only)
- Ethane, λ_{max} = 135 nm, (C-C and C-H bonds, Strength of C-C < C-H)
- Hexane, λ_{max} = 135 nm (ε = 10, 000)

n → σ* (containing O, N, S, X) (λ_{max} 150 → 250 nm)

Compound	λ_{max}(nm)	ϵ_{max}
H_2O	167	1480
CH_3OH	184	150
CH_3Cl	173	200
CH_3I	258	365
$(CH_3)_2S^b$	229	140
$(CH_3)_2O$	184	2520
CH_3NH_2	215	600
$(CH_3)_3N$	227	900

LOW!

n → π*, π → π*

- λ_{max} = 200 -700 (UV-Visible region)
- Unsaturated compounds (double bonds)
- n → π*, low ε value (10-100 M cm^{-1})
- π → π*, strong absorption, ε 1000-10,000 M cm^{-1})

Summary of transitions for organic molecules

- σ → σ* transition in vacuum UV (single bonds)
- *n* → σ* saturated compounds with non-bonding electrons
- λ ~ 150-250 nm
- ε ~ 100-3000 (not strong)
- *n* → π*, π → π* requires unsaturated functional groups (eq. double bonds) most commonly used, energy good range for UV/Vis
- λ ~ 200 - 700 nm
- *n* → π* : ε ~ 10-100
- π → π*: ε ~ 1000 – 10,000

Rule of thumb for conjugation

If greater then one single bond apart

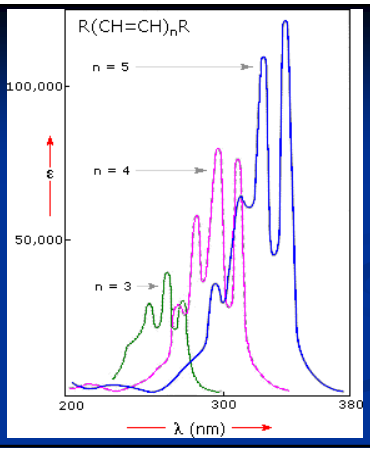
- ε are relatively additive (hyperchromic shift)
- λ constant

$CH_3CH_2CH_2CH=CH_2$ λ_{max}= 184 ε_{max} = ~10,000

$CH_2=CHCH_2CH_2CH=CH_2$ λ_{max}=185 ε_{max} = ~20,000

If conjugated
- shifts to higher λ's (red shift)

$H_2C=CHCH=CH_2$ λ_{max}=217 ε_{max} = ~21,000



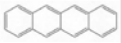
Linear Polyenes

$-(CH=CH)_n-$

n	name	λ_{max} (nm)	ε_{max} (M^{-1} cm^{-1})
1	ethylene	163	?
2	butadiene	217	21,000
3	hexatriene	268	35,000
4	octatetraene	304	?
5	decapentaene	328	120,000

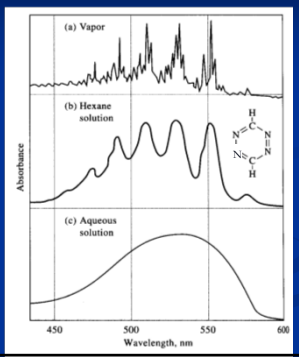
Aromatic Compounds

Linear Fused Aromatics (1)

structure	name	λ_{max} (nm)	ε_{max} (M^{-1} cm^{-1})
	benzene	255	220
	naphthalene	315	320
	anthracene	357	10,000
	tetracene	471	10,000

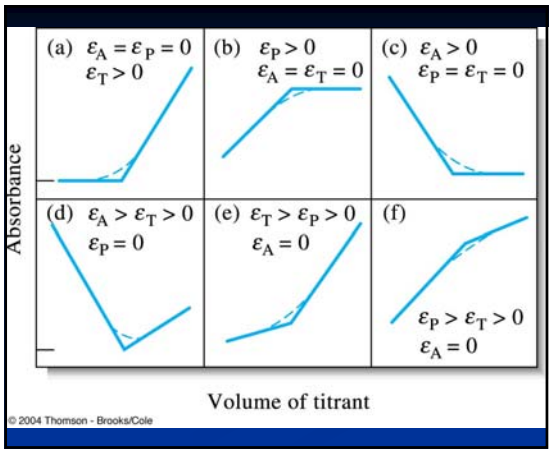
Visible Absorption Spectra

1,2,4,5-tetrazine



Photometric Titrations

- A photometric titration curve is a plot of absorbance as a function of the volume of titrant.
- The spectrometer detects the color change of an indicator allowing the endpoint to be accurately determined.
- For example: titration of an acid and base using phenolphthalein clear → pink
- Plot absorbance as a function of the pH.


(a) $\varepsilon_A = \varepsilon_P = 0$
$\varepsilon_T > 0$
(b) $\varepsilon_P > 0$
$\varepsilon_A = \varepsilon_T = 0$
(c) $\varepsilon_A > 0$
$\varepsilon_P = \varepsilon_T = 0$
(d) $\varepsilon_A > \varepsilon_T > 0$
$\varepsilon_P = 0$
(e) $\varepsilon_T > \varepsilon_P > 0$
$\varepsilon_A = 0$
(f)
$\varepsilon_P > \varepsilon_T > 0$
$\varepsilon_A = 0$
Absorbance
Volume of titrant
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