03-11-19

Spectrophotometry:

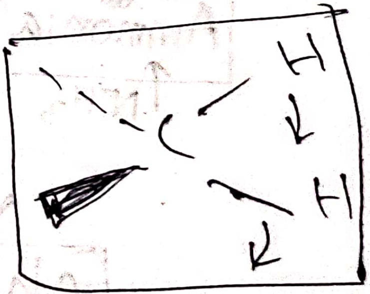
Internal energy
- Kinetic energy (E_K)
- Potential energy (E_P)
  - $E_{(vibration)}$
  - $E_{(Electrical)}$
  - $E_{(rotational)}$
  - $E_{(bond)}$

E_{vib}
- $E_{stretching}$
  - Symmetric
  - Asymmetric
- $E_{bending}$
  - In plane
    - Scissori
    - Rockin
  - Out of plane
    - wagging
    - twisting

Sym:

2850 cm^{-1}

Rock:

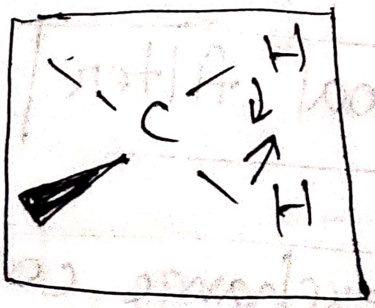


750 cm^{-1}

Asym:

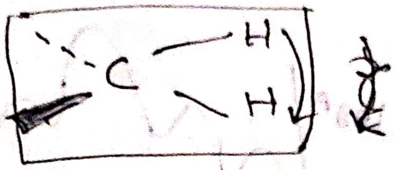
2926 cm^{-1}

Sci:



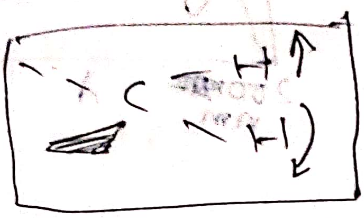
1450 cm^{-1}

wagging:

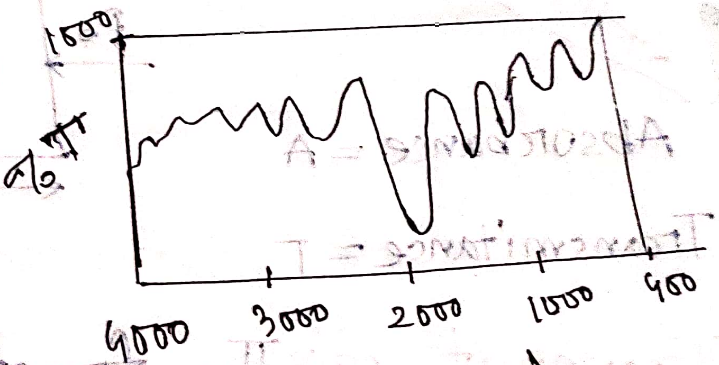


1250 cm⁻¹

Twist



1250 cm⁻¹

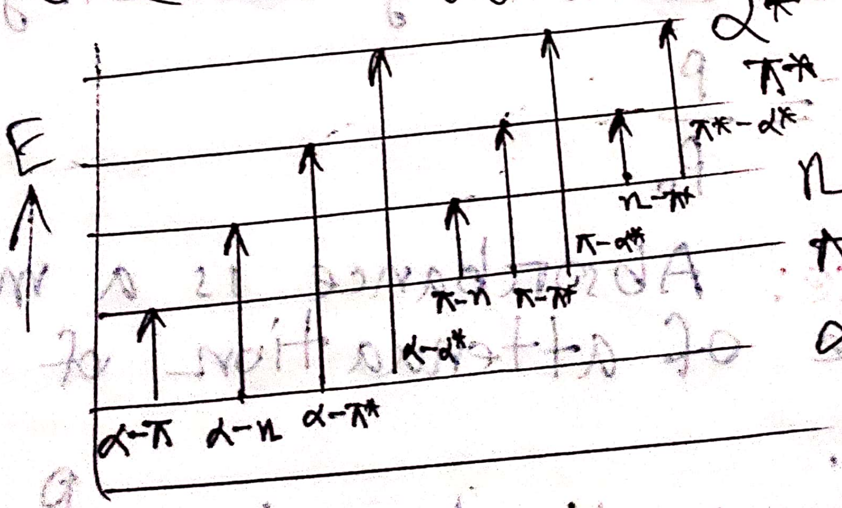


Hooks law:

$$\bar{\nu} = \cancel{8}\frac{1}{2\pi c}\sqrt{\frac{\cancel{K}}{m}}$$

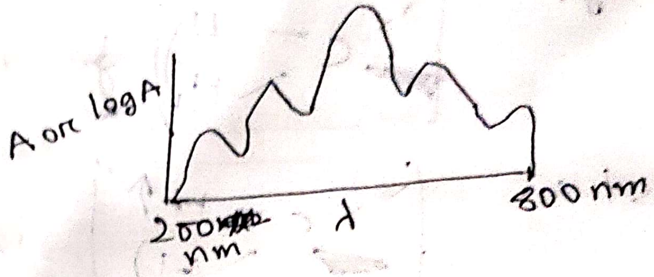
here, $m = \frac{m_1 m_2}{m_1 + m_2}$

Electronic energy level:



bond

A=Absorbance



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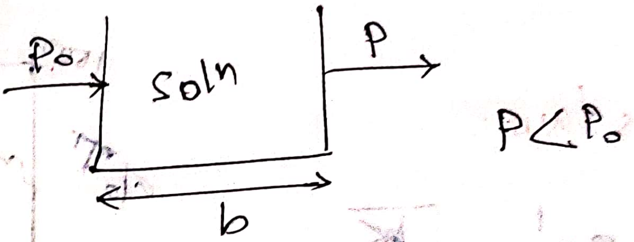


Absorbance = A

Transmitance = T,

Transmitance: The fraction of incident of electromagnetic radiation that was transmitted trough a transparent medium containing absorbing species.

$$T = \frac{P}{P_0}$$

Absorbance: Absorbance is a measure of degree of attenuation of a beam of e.m.r.

$$A = \log \frac{1}{T} = \log \frac{P_0}{P}$$

The measure of decrease of energy by radiation is called Absorbance

* $A = \log \frac{100}{100T}$

$= \log 100 - \log 100T$

$= 2 \log 10 - \log \%T$

$= 2 - \log \%T$

$A = abc$

$A = \epsilon \overset{cm}{b} \overset{mol L^{-1}}{c} \longrightarrow$ Beer law

$\longrightarrow$ For molar solⁿ

a = absorptivity constant

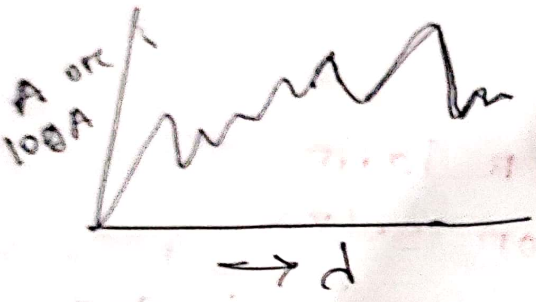
ϵ = molar " "

molar extinction co-efficient

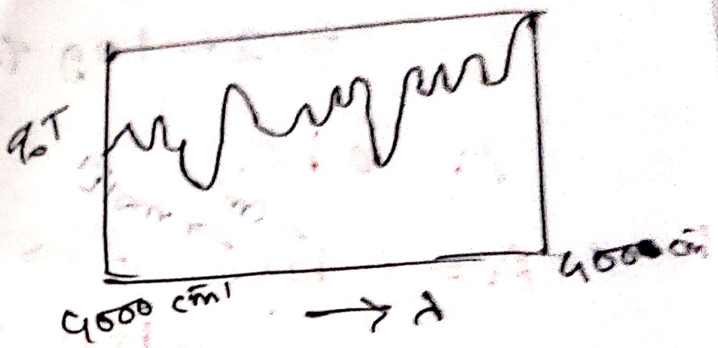
$$\epsilon = \frac{A}{bc} = \frac{1}{cm \ mol L^{-1}} = L \ cm^{-1} \ mol^{-1}$$

Principle of spectrophotometric Analysis:

1. Exitation : $M \xrightarrow{h\nu} M^*$
2. Relaxation : $M^* \longrightarrow M + \text{heat}$.



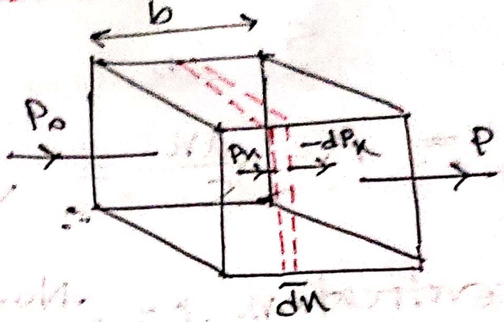
UV



IR

ε	λ	Nature of electronic Transition
$>10^4$	<400 nm	organic group $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, $\sigma \rightarrow$
$10^3 - 10^4$	>400 nm	$L \rightarrow M$, $M \rightarrow L$
$<10^3$	>400 nm	d–d

Derivation of Beer's Law :



no. of particle = n

Area = S

$$ds \propto dn$$
$$= a\,dn$$

Probability of photon capture $= \dfrac{ds}{S} =$

$$= \frac{\text{Target Area}}{\text{Projected area of particle}}$$

$$= \frac{-dP_n}{P_n}$$

$$\therefore -\frac{dP_n}{P_n} = \frac{ds}{S} = \frac{a\,dn}{S}$$

$$\therefore -\int_{P_0}^{P} \frac{dP_n}{P_n} = \int_0^n \frac{a\,dn}{S}$$

$$\Rightarrow -\left[\ln P\right]_{P_0}^{P} = \frac{an}{S}$$

$$\Rightarrow \ln\frac{P_0}{P} = \frac{an}{S}$$

* $V = Sb$

$S = \frac{V}{b}$

$\therefore A = \frac{an}{S} = \frac{an}{V/b} = \frac{abn}{V} = ab\left(\frac{n}{V}\right)$

Concentration, $c = \frac{\text{No. of particles}}{V}$

$= \frac{n \times 1000}{6.023 \times 10^{23} \times V}$ mol/L

$\frac{n}{V} = \frac{6.023 \times 10^{23} \times c}{1000}$ mol/L

$\therefore A = ab \frac{6.023 \times 10^{23} \times c}{1000}$

$= \frac{a \times 6.023 \times 10^{23}}{1000} \times bc$

$\boxed{A = \epsilon bc}$

ϵ → molar absorbtivity

$b \rightarrow cm$

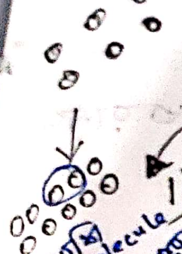
$c \rightarrow mol/L$

$\epsilon \rightarrow L\,mol^{-1}\,cm^{-1}$

$\epsilon = \frac{A}{bc} = \frac{1}{cm \times mol\,L^{-1}}$

☐ Limitations of Beer's law:

1. Beer's law is applicable upto a certain concentration limit.
Validity limit = 0.01 M → 10^{-5} M



Conc. বেশি হলে ২টা molecule কণাটির সাথে বন্ধন গড়ে ফলে যায় e ভিন্ন হতে।

i) Real limitation (0.01 M → 10^{-5} M) — Particle-Particle / hydrogen bonds / Particle-ion interaction
ii) Chemical limitation
iii) Instrumental limitation

• Chemical : Due to association, polymerization, dissociation, temperature effect.

$$* \quad 4\,C_6H_5CH_2OH \xrightarrow{\text{Association and polym.}} (C_6H_5CH_2OH)_4$$

$$* \quad Cr_2O_7^{2-} + H_2O \overset{\text{dissociation}}{\rightleftharpoons} CrO_4^{2-} + 2H^+$$

Orange
$d = 375$ nm

Yellow
$\lambda = 450$ nm

* $Fe^{3+} \overset{temp.}{\rightleftharpoons} Fe^{2+} + e$

λ_1 λ_2

$\lambda_1 \neq \lambda_2$

যাদের assoc., polym., dissoc. হয়না, এধরনের solvent select করতে হবে।

Instrumental:

Due to polychromatic radiation

" " stray

" " Mismatched cell

" " Instrumental noise

assignment → 534 Page (4ta problem)

20-12, 20-13, 20-14, 20-15

27-11-19

Pr. 20.12:

Given value, $C = 4.48$ ppm
$b = 1.00$ cm
$T = 0.309$ $\epsilon = ?$

$$C = 4.48 \text{ ppm} = 4.48 \text{ mg L}^{-1}$$
$$= 4.48 \times 10^{-3} \text{ g L}^{-1}$$
$$= \frac{4.48 \times 10^{-3}}{149} \text{ mol L}^{-1}$$

$$A = \epsilon b c$$

$$\Rightarrow -\log(T) = \epsilon b c$$

$$\therefore \epsilon = \frac{-\log(0.309)}{bc} = 1.69 \times 10^{4}$$

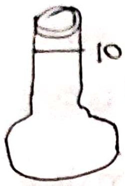
* How to select a wavelength for a particular analyte for UV visible spectrophotometric analysis?

1. Selecting of wavelength in spectrophotometric analysis. (Preparation of stocks so from the std reagent
2. Calibration of instrument
3. Mesurement procedure.

$$C = \frac{m}{M} \cdot \frac{1}{V}$$

$$\Rightarrow 0.01 = \frac{m}{149} \times \frac{1000}{10}$$

$m = \frac{0.01 \times 158 \times 10}{1000} =$



stock soln of $KMnO_4$ using serial dilution method.

A = 0.01 M → এখান থেকে 5 ml নিয়ে 5 ml distilled water conc. তার অর্ধেক হয়ে যাবে.

B = 0.005 M

C = 0.0025 M

D = 0.00125 M

E = 0.000625 M

$B = \frac{0.01}{2} = 0.005$

Procedure.

1. Take 5 ml of stock soln from A to ~~bee~~ B, add 5 ml distilled water and make up to the mark to obtain the conc. of 0.005

. Prepare soln C, D, and E in th same way as described abou

3. Turn on the spectrophotometer, go to action mode

Scan spectrum   photometry   kinetics

Select sacn spectrum mode

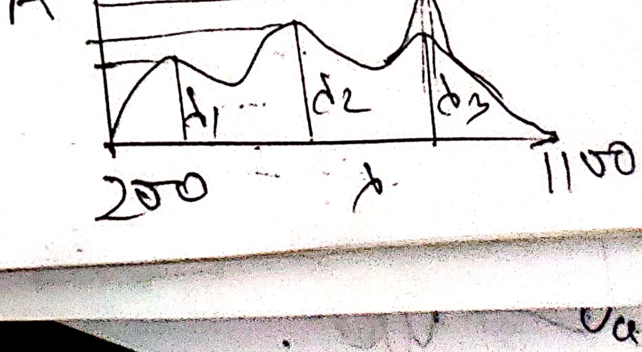
4. Go to parameter selecting

wavelength setting (200nm – 1100nm)

absorbance ~~absolute~~ setting (0.00 – 10.00)

5. Take 4ml due to cell, and place along the direction of radiation path. Click to background correction.

6. Take 4 ml of stock soln from Ⓐ, click to start.



7. From the graph select the wavelength of maximum absorbance.

Calibration of instrument:

$$\epsilon = \frac{A_y}{bc}$$

8. Go to photometric mode and set the parameter as wavelength of d_3 and A(0 - 10.00)

9. Read out the absorbance of stock sol^n of A, b, c, d, e

10. Plot the A vs C graph

11. Read out the absorbance of analyte and calculate the conc. using the eq^n $A = \epsilon bc$.