

10/08/23

classmate

Date \_\_\_\_\_  
Page \_\_\_\_\_

## DNA Structure : Orientation of Glycosidic Bonds

### B-DNA

- helix axis runs thro' centre of each bp (d<sub>run</sub>, d<sub>gyro</sub>)
- bp's stack ⊥ to helix axis (η small, φ, ψ very small)
- Mean helical twist ∼ 36°
- 10 - 10.5 bp/turn
- Deoxyribose C2' endo
- Glycosyl bond → ANTI
- Major groove is wider 12 Å & deeper 8 Å than minor groove (6 Å wide)

### A-DNA

- b.p. centre shifted from helix axis (d<sub>run</sub> 4 Å, d<sub>gyro</sub> 0)
- Inclination → η 20°
- Mean helical twist ∼ 26.5°
- 11 bp/turn
- Deoxyribose C3' endo.
- Glycosyl bond → ANTI
- Major groove is narrow & deeper than minor groove than minor groove NOT DEEP.

### RNA

mRNA

tRNA

rRNA

diff b/w Guanine in DNA and RNA ?? → because of hydroxyl group which causes steric hindrance

Z-DNA → Left Handed

- bp centre shifted from helical axis ( $\Delta x \approx -3\text{ Å}$   $\Delta y \approx +25\text{ Å}$ )
- Inclination →  $\eta = 7^\circ$ .  $52^\circ$  - G/C step  
 $6^\circ$  - C/G step
- Mean helical twist  $52^\circ \approx 60^\circ$  per dimer (---G-C-G-C-G-C---)  
 dinucleotide
- 12 bp/turn
- Deoxyribose : C2' endo at C  
 C3' endo at G
- Glycosyl bond → ANTI for C : syn for G (alternative C9 seg.)
- Major groove budes out & minor groove is narrow & deep.

### Hydration & ions

role on structure of DNA

A-DNA

→ low humidity (stable in)

→ why water is playing role → it phosphate ion in DNA tend to be solvated.

So, 1

$\text{Na}^+$  → can stable phosphate groups

→ screen the charge to bring phosph. gp.

Closer.

→ low humidi.

→ high [salt]

- large anti organic solvent.

DNA binds to DNA to remove the water. Which ↑ entropy. Water will go away from DNA. Preferential Binding site.

DNA - Protein Interactions

- Regulatory → Packaging
  - proteins that bind to promoter and enhancer regions of genes, influencing the recruitment of RNA polymerase and initiation of transcription.
- Replication
  - enzymes involved in DNA Replication and repair, such as DNA Polymerase and DNA Ligase also interacts with DNA
- DNA repair Help proteins called Rad51 and Rad51 Orchestrates HR helps in DNA repairing
- ~~Recombination~~ → DNA goes recombination / shuffling.
  - Ex: Many brothers & Sis. are same.
  - Mitotic Recombination** → creates genetic diversity.
- DNA Binding Motif → Some conformation in DNA which favors DNA-protein interaction.
  - A DNA binding motif is a specific protein structure or sequence motif that enables a protein to interact with DNA in a sequence-specific manner.
  - TATA-box → transcription
  - DNA motif.
  - called as Goldberg-Hogness box.
- Packaging.

- { how DNA-protein interaction is stable ?  
 how protein knows where to bind in DNA ?  
 how you tolerate mutation ?  
 Evolutionary trends ??

→ Structural Stability & Biological aspect of DNA-protein interactions.

Twisting & Winding of DNA  
strands among themselves.

Persistence length

models the DNA

using polymer statistical mechanics

minimum DNA length at  
which the directionality  
is maintained

## DNA Supercoiling

(-writhe) (+writhe)  
Negative & Positive Supercoiling

Topoisomerase

The LN provides a measure of how two DNA strands are wound around each other for a double helix. (Twist + writhe = linking number)

DNA Gyrase  $\rightarrow$  Negative Supercoiling  
bacterial

Topology

Linking number

No. of turns  
or rotations  
of one DNA strand  
around another  
double helix

(W) Writhe

Degree of coiling or twisting of a three dimensional object

DNA strands are twisted around each other in a manner that introduces additional coils or turns into double helix structure.

can result in positive supercoiling or negative supercoiling

→ necessary for compacting DNA in cell.

(N+3/3) Intertwined Supercoil

Solvent-wrapped Supercoil

In Eukaryotes DNA wraps around a core of histone proteins to form chromatin fiber. Chromosomes are made up of dense chromatin fibers, shown here in the metaphase stage.

Topoisomerase-II

present in eukaryotes

DNA supercoiling

Chromosome condensation

Duplex DNA  $\rightarrow$  diameter: 2.4 nm

up of dense chromatin fibers, shown here in the metaphase stage.

## DNA in the cell

Watch Shonks Biology on DNA Supercoiling

## Polymers Elasticity and Collapse

### Conformational Entropy

### Random Flight Model

#### (a) Linear Polymers

Real Chain  $\rightarrow$  Stiffness bending correlations

$$\sqrt{\langle \delta^2 \rangle} = \sqrt{N \cdot b}$$

$$\langle \delta^2 \rangle = n b^2$$

No. of C-C bonds

Degree of Polymerization = DP  $= n_{1/2}$

#### Chain Stiffness

Angular correlations

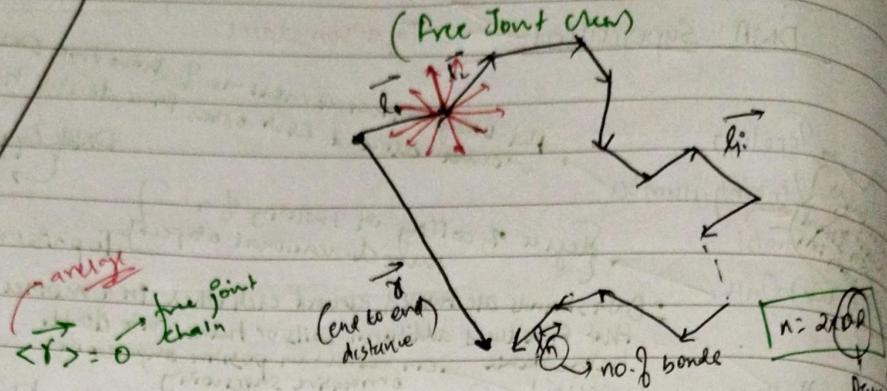
$$\cos \theta \propto \sqrt{M}$$

classmate  
Date \_\_\_\_\_  
Page \_\_\_\_\_

$$\left\{ \begin{array}{l} \delta_{rms} = \sqrt{\langle r^2 \rangle} \\ h_{rms} \approx \sqrt{M} \end{array} \right\}$$

Molecular weight & molar mass chart

$$\sum \vec{r} = 0$$



$\propto \langle r^2 \rangle \propto N^2$  "straight rod"  
 $\propto \langle r^2 \rangle \propto N$  "freely jointed chain"

$N = \text{no. of C bonds}$

$$\delta_{rms} = \sqrt{\langle r^2 \rangle} = \sqrt{L^2 + T_{avg}} = b\sqrt{N}$$

$$\langle r^2 \rangle = \langle \sum \vec{r}_i^2 \cdot \sum \vec{r}_j^2 \rangle$$

$$\approx \int \langle r^2 \rangle = Nb^2 + 2Nb^2\gamma$$

$$= b^2N(1+2\gamma)$$

$$D.P. = M/M_0$$

(ii) L

Radius of gyration  $\propto h_{rms}$

$$\propto \sqrt{N}$$

$$R_g = 0.3\sqrt{M} (\text{Å})$$

Chain Stiffness  $\longleftrightarrow$  Angular Correlation

$$\langle r^2 \rangle = C_w N b^2$$

Characteristic Ratio

$$C_w > 1$$

- $C_w = 1 \rightarrow$  free joint
- $\approx 2 \rightarrow$  free rotation (fixed bond angle)
- $\approx 3 \rightarrow$  Hindered rotation

## Kuhn Model

$$\langle r^2 \rangle = C_w N b^2 = N_k b_k^2$$

$$\left\{ \begin{array}{l} b_k \\ N_k \end{array} \right.$$

Watch Gaussian coil & statistical segment lengths Associate  
by Prof. Rakesh Polymer Chemistry

$$L = N_b \cos \psi \approx N_b b_k$$

$$\frac{N_b b_k^2}{N_b b_k} \approx \frac{C_w N_b^2}{N_b \cos \psi}$$

$$\frac{b_k}{b} \approx \frac{C_w}{\cos \psi}$$

$$\frac{N_b}{N} \rightarrow \frac{b \cos \psi}{b_k} \approx \frac{\cos^2 \psi}{C_w}$$

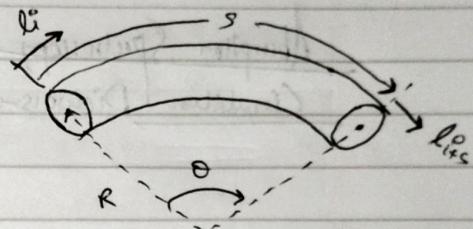
### Persistence Length ( $\xi_p$ )

$$g(s) = \frac{\langle l_i \cdot l_{i+s} \rangle}{b^2}$$

$$= \langle \cos \theta(s) \rangle$$

$$g(s) \approx e^{-s/\xi_p}$$

$$\xi_p = \frac{k_b}{RT} \approx 0.6 C_w / \text{mol}$$



(Degree of Polymerisation (DP)  $\propto$  Number of Bonds ( $n$ ))

# Spectroscopy

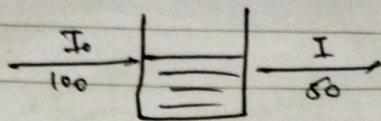
UV-VIS Spec

CD Spec

Fluorescence Spec

Mass spectrometry

ITC

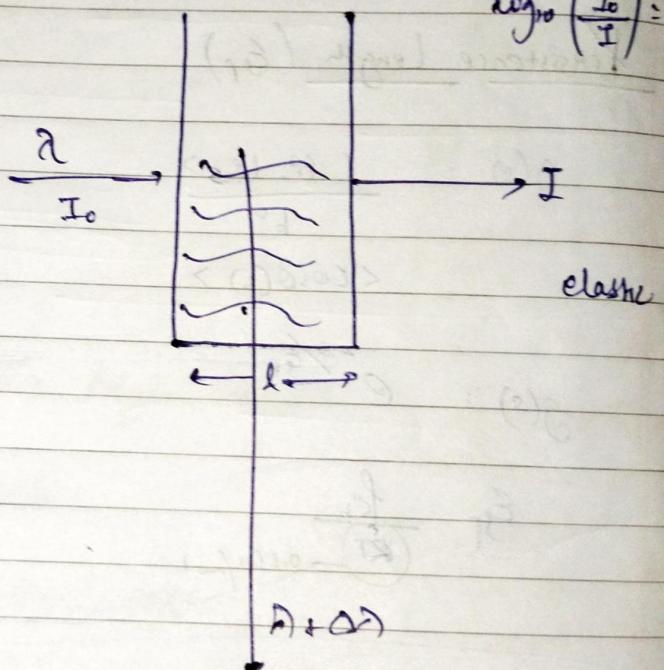
~~Notes~~UV-VIS Spec

$$\text{Absorbance} = \log_{10} \left( \frac{I_0}{I} \right) = 0.3010$$

Absorption Spectroscopy  
Circular Dichroism

$$A = E_c C d$$

$$A_L - A_R : CD$$



$$\log_{10} \left( \frac{I_0}{I} \right) = 4$$

Techniques:

2/08/23

classmate

Date \_\_\_\_\_

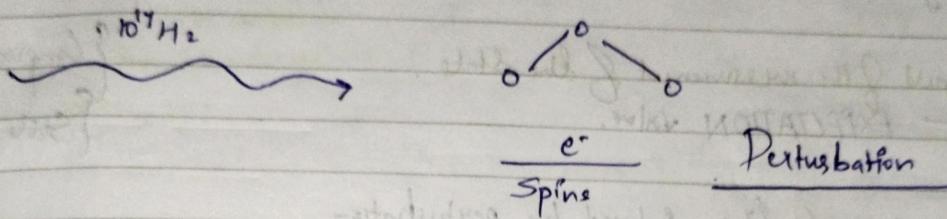
Page \_\_\_\_\_

## Tutorial 2

### • Circular Dichroism

~~Notes~~

### Absorption



### Questions Asked

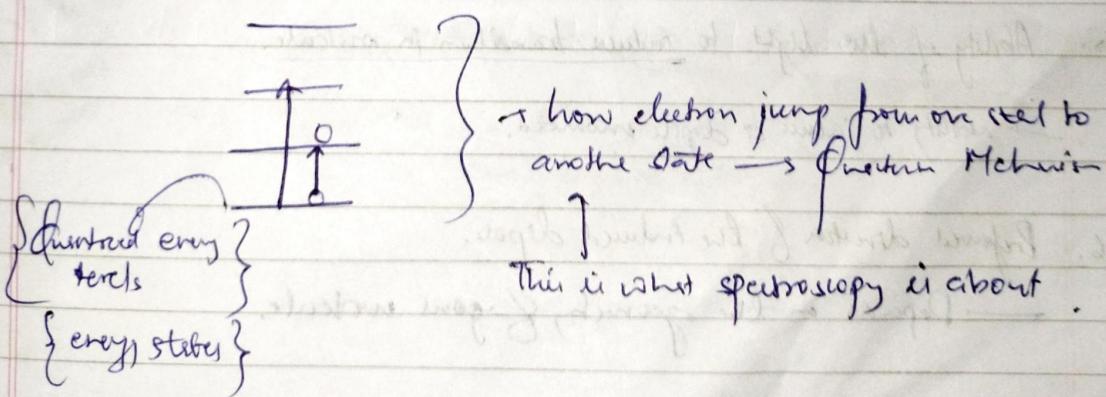
#### ↳ Rate of Perturbation.

Rate at which mol. absorbs the light.  $\rightarrow$  Time taken by photons goes to higher energy state  
↳ responses to perturbation.

↳ Why Only certain wavelengths cause change in the state of mol.

↳ How the presence of molecules alters radiation.

To understand the properties of molecules, we need to study quantum mechanics.



## Postulates of Quantum Mechanics

1. State of System described by wavefunction.

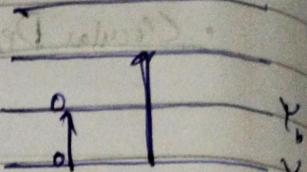
2. Operator to act on wave function

Why → to measure an observable quantity.

(i) Energy

(ii) Dipole moment

• governed by an Operator.



} wave function  
 is the representation  
 of e. Planck energy  
 state.  
 } Complex Number  
 } State function

3. Result of the measurement of the state.

→ EXPECTATION value.

4. Transition from states induced by perturbation

→ This can be measured by the Operator.

The effectiveness of the transition  $\rightarrow$  Probability from State A to State B

$\Psi_b$

$\Psi_a$

5. Ability of the light to induce transition in molecule.

→ ability to induce a dipole moment.

6. Preferred direction of the induced dipole.

→ Depends on the geometry of your molecule.

Properties of wave function

Complex number  
time dependent  
related to the probability of finding your system in a particular state or position.

position, spin

presence of external field

How?

position, spin.

↳ By taking squares  $\rightarrow P = \Psi^* \Psi$

Probability can be computed by squaring the  $\Psi$  function (amplitude) for that position, spin.

$P = \Psi^* \Psi$   
prob.

$\rightarrow \langle \Psi | \Psi \rangle$

implies  $\int p d\tau = 1$

$\int \Psi^* \Psi d\tau = 1$

Then the Wave function is normalized

(a)  $P \rightarrow \langle \Psi_a | \Psi_a \rangle = 1$  }  $\rightarrow$  normalisation of the wavefunctions that obey them are called normalized wavefunctions.

(b)  $P \rightarrow \langle \Psi_b | \Psi_b \rangle = 1$  }

$\langle \Psi_a | \Psi_b \rangle$  }  $\rightarrow$  overlap integral

overlap integral

$\rightarrow$  Projectors of a to b. (measures the projection) (pure numbers)

$\rightarrow$  give the similarity of two states.

(ii)  $\langle \Psi_a | \Psi_b \rangle = 0 \rightarrow a \& b \text{ can't be projected}$

$\hookrightarrow a \& b \text{ are orthogonal.}$

$\langle \Psi_a | \Psi_b \rangle = \Psi_a^* \Psi_b$   
if  $\Psi_a^* \Psi_b$  are considered vectors

$$\langle \Psi | \Psi \rangle = 1$$

$$\Psi = C_a \Psi_a + C_b \Psi_b$$

↳ linear combination of two wavefunctions

Eigen Value  $E_\alpha$

any state that  
satisfies this eqn'  
is called an  
eigenstate.

$$\text{Operator } \hat{O} \Psi = (\lambda) \Psi \quad \text{number} \rightarrow \text{the eigenvalue.}$$

Properties of the system can be calculated by examining the effect of various mathematical operations on the wavefunction.

eq 7.7

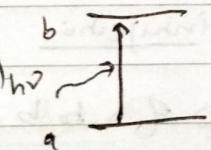
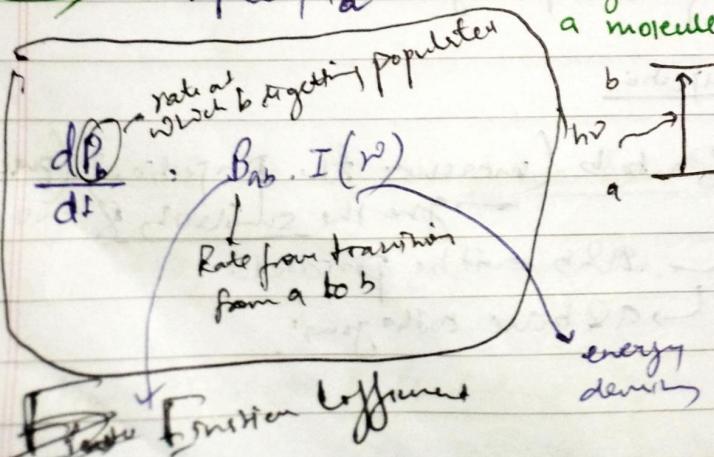
$$\begin{aligned} \underline{\langle O \rangle} &= \int \Psi^* \hat{O} \Psi d\tau = \langle \Psi | \hat{O} | \Psi \rangle = \langle \Psi | \lambda | \Psi \rangle \\ &= \langle \Psi | \Psi \rangle \lambda \\ &= \lambda \end{aligned}$$

{ The Expectation Value  
Observable quantity }

Transition Dipole moment ( $M_{ba}$ )

{ So if  $\Psi$  satisfies eq 7.7 then b is  
Observed quantity & will be 1. }

$\langle \Psi_b | M | \Psi_a \rangle \rightarrow$  This integral describes the ability of light to distort a molecule in state a so as to produce elements



$$B_{ab} = \left( \frac{2}{3} \right) \left( \frac{\pi}{4} \right) \left| \langle \psi_b | \mathbf{z} | \psi_a \rangle \right|^2$$

$B_{ab}$  is the transition rate per unit energy density of the radiation and  $I(v)$  is the energy density incident on the sample at frequency  $v$ .

### UV-VIS Absorption Space

$$\frac{n_a}{n_b} = \exp \left( -\frac{\Delta E}{RT} \right)$$

~~for absorption~~ ~~b~~

~~at equilibrium in front of lamp~~ ~~a~~

$\Delta E$  electronic States

$$S_0 - S_1 = 80 \frac{\text{Kmol}}{\text{mol}}$$

$$Vib = 10 \frac{\text{Kmol}}{\text{mol}}$$

$$\text{Rot.} = 1 \frac{\text{Kmol}}{\text{mol}}$$

Dynode chain → multiplies the electrons when ~~hit~~ with electrons.

accelerate

Date \_\_\_\_\_  
Page \_\_\_\_\_

## Measuring Light Absorption

Mono-

(a) Source (Xenon or He)

Monochromator

$\frac{\lambda}{I_0}$

$\frac{c}{l}$

principle → Photoelectric effect

(Photomultiplying tube)

Detector

Amp

Beam Splitter -

Diode Array detector

Solvent broadening, Doppler broadening

- Effect of solvent on wavelengths

$$\text{Population Ratio} = e^{\frac{-\Delta E}{kT}}$$

$\Delta E \rightarrow$  Energy gap  
 $k \rightarrow$  Boltzmann constant ( $8.647 \times 10^{-5} \text{ eV/K}$ )  
 $T \rightarrow$  Temperature

classmate

### Tutorial-3

$$1 \text{ Da} = 1 \text{ g/mol}$$

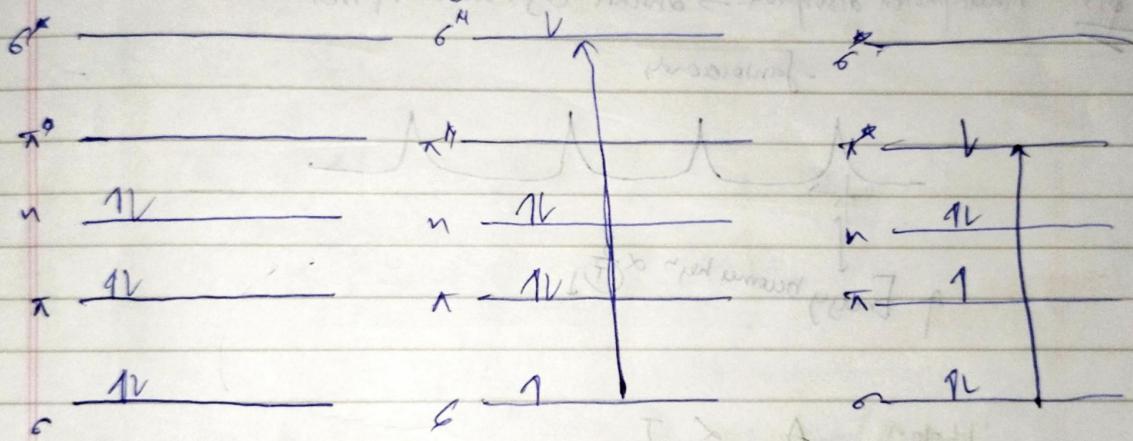
$$D_{ab} = |\langle \psi_b | \psi_a | \psi_a \rangle|^2$$

$$= 9.18 \times 10^3 \int \left( \frac{\epsilon}{\nu} \right) d\nu \underbrace{(\text{d}e/\nu)^2}_{\text{S. Energy} \times \text{dissoc}}$$

Obs. Strength

$$f_{ab} = \left( \frac{8\pi^2 m_L}{3h\nu} \right) D_{ab}$$

$$= 4.315 \times 10^7 \int \epsilon(\bar{\nu}) d\bar{\nu}$$



- Frank Condon Principle (no nuclear motion)



Born-Oppenheimer Approximation

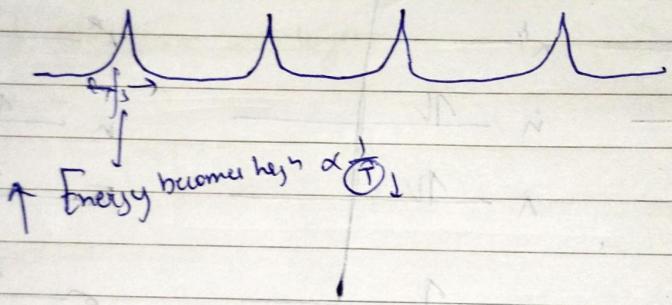
Laser wavefunctions

$$\Psi(r_1, r_2, \dots, r_n, R_1, \dots, R_m)$$

$$= \Psi^{\text{electronic}}(r_1, \dots, r_n, R_1, \dots, R_m) \\ \times \phi^{\text{vib}}(R_1, \dots, R_m)$$

QPSMulti-photon absorption  $\rightarrow$  Antenna light source required

femtoseconds



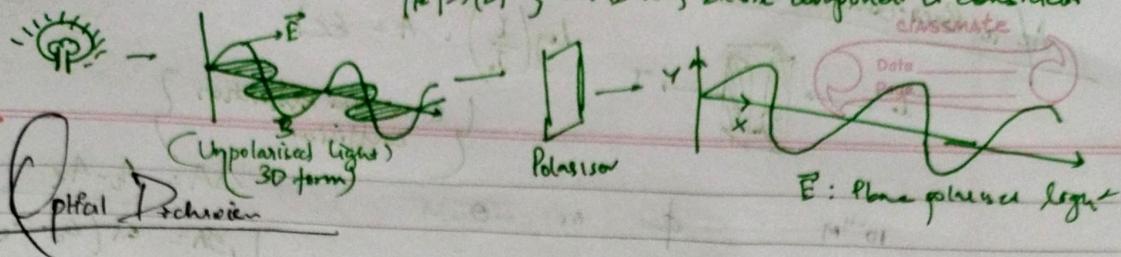
$$I_{\text{photon}} \propto A \propto I$$

$$I_{\text{photon}} \propto A \propto I^2$$

Advantage  $\rightarrow$ 

→ PEM  
Photovoltaic modules  
Converts linear plane  
polarized into circular polarized  
light.

30/08/23



### Different Manifestations

- Optical Rotatory → Plane polarized light passed through a sample.

- Ellipticity → Optical Active sample, passed by plane polarised light

$$\theta = \tan^{-1} \left( \frac{\text{minor}}{\text{major}} \right)$$

*(Left Polarized light)      (Right Polarized light)*

$\vec{E} = E_0 \sin \omega t$

$$\vec{E}_e = \frac{1}{2} [E_{0\text{sin}} + j E_{0\text{cos}}]$$

$$\vec{E}_r = \frac{1}{2} [i E_{0\text{sin}} - j E_{0\text{cos}}]$$

$$\omega = 2\pi f$$

### Linear & Circular Dichroism

$$\text{Circular Dichroism} = (A_L - A_R)$$

*measures the colour*

- Circular Birefringence

$$(n_L - n_R)$$

*differ in L&R optical refractive*

$$\text{Difference in Absorption} = CD$$

*in Anisotropic medium*

O-R-P

Optical Rotatory Distortion      Optical Rotatory Distortion

Ability of an optically active compound to rotate the polarised light anticlockwise or clockwise direction.

$$\begin{aligned} \text{for } \leftarrow 180 (n_L - n_R) \text{ deg.} \\ \text{for } \rightarrow 2.303 (A_L - A_R) \cdot 180 \text{ deg.} \end{aligned}$$

Absorbance

Spectropolarimeter → measures ORD

Ap to Beer-Lambert Law

$$\log\left(\frac{I}{I_0}\right) = A = \epsilon c l$$

$\epsilon$  molar extinction coefficient

$$10^{-4} M \quad \phi \quad \text{or} \quad \theta$$

$0.1 - D_{-1}$

$$\Delta A = A_i - A_e$$

$$\Delta A = \epsilon l (\epsilon_i - \epsilon_e)$$

for unit concn & path length.

$$\{\Delta E = \frac{\Delta A}{c l}\}$$

Molar Optical Rotatory Power  $[\alpha]$ :

$$\frac{100. \phi}{c l}$$

Molar Ellipticity  $[\theta]$ :

$$\frac{100.0}{c l}$$

$$[\theta] = 8300 \Delta E$$

difference in wavelength in left & right optics

### Kronig-Kramen Transform

#### App. of CD

- determines secondary structure of proteins  $\alpha$ -Helix &  $\beta$ -Sheet
- folding & unfolding of protein
- heat, pH, solvent
- Hormones, proteins, polysaccharides
- Ligand Binding changes

#### CD signal

Rotation strength

$$R_{\text{CD}} = \frac{3hc}{2\pi^3 N_0} \int \left( [\theta(\lambda)] \right) d\lambda$$

Rosenfeld in 1988

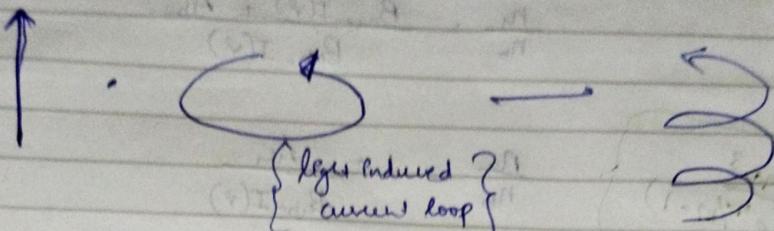
$$R_{\text{CD}} = \text{Prey} \left( \langle \psi_0 | \mu | \psi_n \rangle - \langle \psi_n | \mu | \psi_0 \rangle \right)$$

$$m = \left( \frac{e}{dm} \right) (r \times t)$$

Orbital Angular Momentum

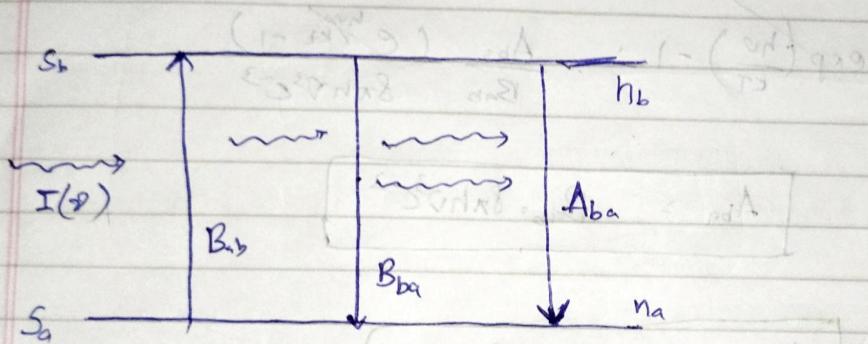
measure of circulation of charge.

Precipitate Deposit movement: Magnetic Digr. & Monitors



Helical sense  
(Only in asymmetric structures)

### Fluorescence Spectroscopy



$$\frac{n_a}{n_b} \approx e^{-\frac{(E_a - E_b)/kT}{h\nu/kT}} = e^{+\frac{h\nu}{kT}}$$

$(A \rightarrow) g_{a,g} \cdot (A)$

$$n_a B_{ab} I(\nu) = n_b B_{ba} I(\nu) + n_b A_{ba}$$

$$\frac{n_a}{n_b} \rightarrow \frac{B_{ba} \cdot I(\nu) + A_{ba}}{B_{ab} \cdot I(\nu)}$$

$$I(\nu) = \frac{8\pi h\nu^3}{c^2(e^{h\nu/kT} - 1)}$$

$$\frac{n_a}{n_b} = 1 + \frac{A_{ba}}{B_{ab} \cdot I(\nu)}$$

$$\exp\left(\frac{h\nu}{kT}\right) \approx 1 + \frac{A_{ba}}{B_{ab}}$$

Boltzmann's const.

$$\frac{n_a}{n_b} = \exp\left(\frac{h\nu}{kT}\right)$$

$$\exp\left(\frac{h\nu}{kT}\right) = 1 + \frac{A_{ba}}{B_{ab}} \cdot \frac{(e^{\frac{h\nu}{kT}} - 1)}{8\pi h\nu^3 c^3}$$

$$\exp\left(\frac{h\nu}{kT}\right) - 1 = \frac{A_{ba}}{B_{ab}} \cdot \frac{(e^{\frac{h\nu}{kT}} - 1)}{8\pi h\nu^3 c^3}$$

$$B_{ab} = \frac{(2\pi)^3}{(2h)^3} D_{ab}$$

$$A_{ba} = B_{ab} \cdot 8\pi h\nu^3 c^3$$

$$A_{ba} = \frac{32\pi^3 \nu^3}{3h} \cdot D_{ab}$$

$$\frac{dn_b}{dt} = -A_{ba} \cdot n_b$$

$$n_b(t) = n_b \exp(-A_{ba} t)$$

$$A_{ba} = k_F$$

$$k_F = A_{ba} = \frac{1}{2\pi}$$

$$T_c = \frac{1}{A_{ba}}$$

$$\left[ \phi_r = \frac{k_r}{k_r + k_{nr} + k_{is} + k_q(Q)} \right]$$

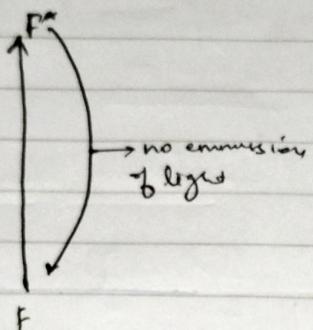
~~6/8 alternative  
MPA Semibasic~~

$$\begin{aligned} & \text{Fluorescence yield} \\ & \phi_r = \frac{k_r}{k_r + k_{nr}} \end{aligned}$$
  

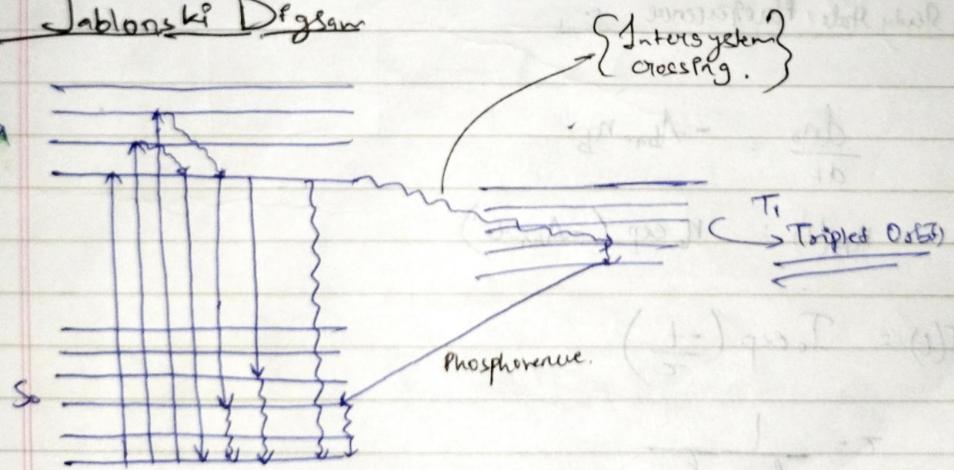
$$\begin{aligned} & \text{Fluorescence lifetime} \\ & \tau = \frac{1}{k_r + k_{nr}} \end{aligned}$$

$k_r$  → rate constant for radiative decay.  
 $k_{nr}$  → rate constant for non-radiative decay.

Radiative and non radiative component?



Jablonski Diagram



Absorption and Emission Spectra

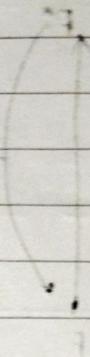
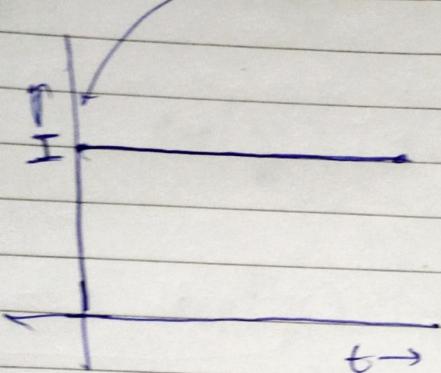
## Fluorescence

- Steady State
- Time-resolved

Fluorescence  $\propto$  Value of  $F^*$  (Population)

Steady state  $\rightarrow$  Population of  $F^*$

Fluorescence Intensity



Outline

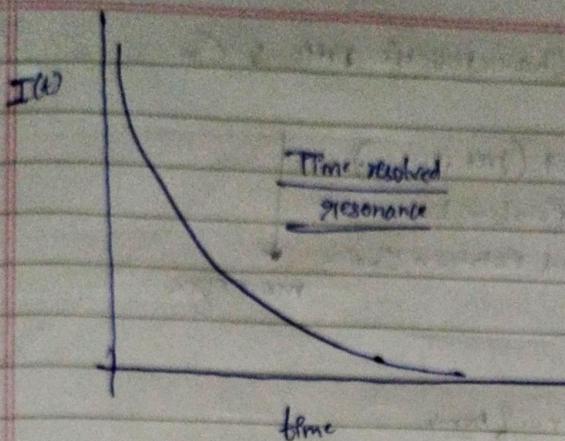
Measuring Steady State Fluorescence

$$\frac{dn_b}{dt} = -A_{ba} \cdot n_b$$

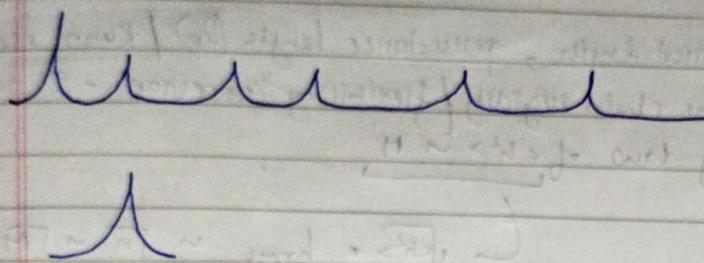
$$n_b(t) = n_b \exp(-A_{ba} \cdot t)$$

$$I(t) = I_0 \exp\left(\frac{-t}{\tau}\right)$$

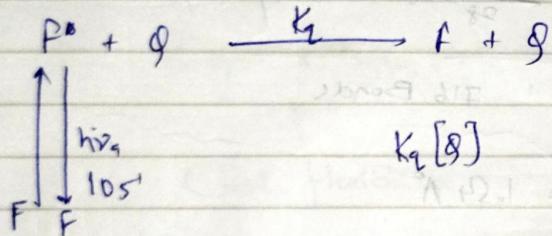
$$\tau = \frac{1}{k_r + k_{nr}}$$



Time resolved  
resonance



### Solvent Relaxation



$$k_2[\text{S}]$$

$$\phi = \frac{k_x}{k_{1c} + k_2[\text{S}] + k_{1sc} + k_x}$$

$$c = \frac{k_x}{k_{1c} + k_2[\text{S}] + k_{1sc} + k_x}$$

## Concept of Chain flexibility - Characteristic ratio, $C_0$

$$\langle h^2 \rangle = \begin{cases} n.l^2 & \rightarrow \text{Straight (free joint)} \\ 2nl^2 & \rightarrow \text{freely Rotatable} \\ 3nl^2 & \rightarrow \text{Hindered Rotatable} \end{cases}$$

more rigid

$$\langle h^2 \rangle = C_0 nl^2$$

depends on no. of bonds

Characteristic ratios, statistical length, persistence length ( $\ell_p$ ) / Kuhn length ( $\ell_K$ ) are all about the chain rigidity / flexibility "correction" - It does not change the scaling law of  $\langle h^2 \rangle \propto M$ ,

$$\sqrt{\langle h^2 \rangle} = \text{length} \propto \sqrt{n} \propto \sqrt{M}$$

\* PF (Polyethylene)  $C_0 = 7.4$   $\{ \text{CH}_2\text{CH}_2\}_n$

$$M = 10,000 \text{ g/mol}$$

$$M/M_0 = D.P = \frac{1000}{28} = 85.7 \text{ Repeating Unit}$$

$$\therefore n = 2 \times DP = 716 \text{ Bonds}$$

$$\lambda = |\vec{r}|_{C-C} = 1.54 \text{ \AA}$$

$$\begin{aligned} \therefore \langle h^2 \rangle &= C_0 \cdot n l^2 \\ &= (7.4) (716) (1.54)^2 \end{aligned}$$

$$\therefore \sqrt{\langle h^2 \rangle} = \text{length} = 112 \text{ \AA} \approx 1.12 \text{ nm}$$

Statistical Segment length and DP (Degree of Polymerizations)

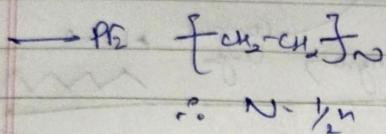
$$\langle h^2 \rangle = C_{av} n \cdot b^2 \leftarrow (\# \text{ of bonds})$$

OR

$$\therefore N_b \leftarrow (\text{No. of Repeating units})$$

statistical segment length

①



$$C_{av} n \cdot b^2 = \frac{1}{2} \cdot N_b \cdot b^2$$

$$\therefore b^2 = 2 C_{av} n \cdot b^2$$

$$\boxed{\therefore b = \sqrt{2 C_{av} n} \text{ Å}}$$

1.54 Å

PLS 11

②

$C_{av} \leq b$   $\Rightarrow$  It is preferred because

How will u calculate  
the bond length in

$\text{f}_{\text{CH}_2\text{O}} \text{f}_{\text{CH}_2}$ ?  
 $[\text{H}_2\text{O}] \text{f}_{\text{CH}_2}$

Defines a length scale

Chain flexibility

$b$  = Statistical Segment length ( $\text{Å}$ )

$$N = D.P.$$

$$\boxed{\langle h^2 \rangle = b N}$$

\* P.E 10,000 g/mol

$$M/N_D + 38 \quad RV_s = N$$

$$\boxed{\langle h^2 \rangle = n \cdot b^2} = 38 \cdot (5.9)^2 = 12,000 \text{ Å}^2$$

$$\text{Thom} = \sqrt{h_{\text{avg}}^2} = \sqrt{12,000} = 11,24 \text{ Å}$$

Kuhn length / Persistence length & n (frag bonds) ( $l_k = 2l_p$ )

Persistence length

$$\vec{l} = \sum_{i=1}^n \vec{l}_i$$

$$\vec{l}_p = \left( \frac{1}{n} \vec{l} \cdot \vec{l} \right)$$

$$= \left( \frac{1}{n} \vec{l}_1 \cdot \sum_{i=1}^n \vec{l}_i \right)$$

$$\vec{l}_p = \frac{1}{n} \left\{ (\vec{l}_1 \cdot \vec{l}_1) + (\vec{l}_2 \cdot \vec{l}_2) + \dots + (\vec{l}_n \cdot \vec{l}_n) \right\}$$

$$\boxed{l_k = 2l_p}$$

$l_k = \text{Kuhn length}$

$$l_k = \frac{\langle \vec{l} \cdot \vec{l} \rangle}{L}$$

$$\boxed{\frac{n l^2}{L} = l_k}$$

contour length  
stiffness

$L = n l$

$$l_k = \frac{\langle \vec{l} \cdot \vec{l} \rangle}{L} \quad \xrightarrow{\text{cont. l.}} \quad \frac{\text{cont. l.}}{L}$$

$$\therefore l_k = \text{cont. l.}$$

$$l_k = 2l_p$$

$$l_p = \frac{1}{2} l_k = \frac{\text{cont. l.}}{2}$$

07/07/23

$$F(\lambda) =$$

$$\log\left(\frac{I_0}{I}\right) \propto E.C.l$$

$$\ln\left(\frac{I_0}{I}\right) \propto -2.303 E.C.l$$

$$\frac{I_0}{I} \propto e^{-2.303 E.C.l}$$

$$\frac{I_0}{I} \propto e^{-2.303 E.C.l} \quad \text{absorbance}$$

$$\frac{I_0}{I} = I_0 [1 - 2.303 E.C.l]$$

$$I_0 - I = 2.303 I_0 E C l$$

$$\left\{ e^x = 1 - x + \frac{x^2}{2!} - \dots \right\}$$

$$F(\lambda) \propto 2.303 E.C.l I_0$$

$$\propto 2.303 E.C.l I_0 \cdot f(\lambda), d$$