SPECTROSCOPY – 1 UNIT 3 PG 1ST SEMESTER PRIYANKA BARUA

UV-VISIBLE SPECTROSCOPY

Interaction of EMR with Matter

- Two types of interaction are exploited as the basis of the methods we will be looking at.
 - Absorption light is absorbed by an atom, ion or molecule, taking it to a higher energy state.
 - Emission the release of a photon by an atom, ion or molecule, taking it to a lower energy state.



 $\boldsymbol{\epsilon}$ is called molar absorptivity

The absorption process

Absorption of light is a complicated process.

Each electronic state is subdivided into a number of vibrational sub-levels.

In turn, each vibrational sub-level is further divided into rotational sublevels.



FIGURE 7.2. Molecular energy levels and (a) electronic, (b) rotational, and (c) vibrational transitions.



Figure 6.10 (a) Relative energy levels of bonding, antibonding, and *n* electrons. (b) Transition of ground-state σ , *n*, and π electrons to σ^* and π^* orbitals.



FIGURE 7.3. Ultraviolet absorption spectra of benzene. Upper: Benzene solution in ethanol solvent. Lower: Benzene vapor. From R. E. Dodd, Chemical Spectroscopy. Amsterdam: Elsevier, 1962, p. 227, by permission of the publisher.

Collisions between molecules lead to broadening of absorption bands

n → σ* transitions

The compound must contain atoms with unshared electron pairs.

Compounds containing O, S, N and halogens can absorb via this type of transition.

Absorptions are typically in the 150-250 nm region and are not very intense.

 $\lambda_{\max} CI < \lambda_{\max} Br < \lambda_{\max} I$

Table 7–1 Some Examples of Absorption Due To $n \rightarrow \sigma^*$ Transitions ^a		
Compound	$\lambda_{\max}(nm)$	Emax
H ₂ O	167	1480
CH ₃ OH	184	150
CH ₃ Cl	173	200
CH ₃ I	258	365
(CH3)2Sb	229	140
(CH3)2O	184	2520
CH ₃ NH ₂	215	600
(CH ₃) ₃ N	227	900

n -> π^* and π -> π^* transitions

n -> π^* and π -> π^* transitions	Examples	λ_{max} , nm	Emax
For a π^{*} orbital to be available, there must be some degree of unsaturation multiple bonds and resonance structures	Alkenes	177	13000
	R-C=C-C=C-R	217	21000
	Alkynes	178	10000
These result in some of the most intense absorptions (200 - 700 nm region).	Carbonyls	186	1000
	Carboxylic acids	204	41
As the degree of unsaturation increases, you	Nitro	280	100
typically see a shift to higher λ .	Aromatic	204	7900
$\longrightarrow \pi^*$ transitions occur at longer wavelengths			

n

TABLE 7.3. Electronic Energy Levels and Transitions

Transition	Region of Electronic Spectra	Example
$\sigma \rightarrow \sigma^*$	Vacuum ultraviolet	CH ₄ at 125 nm
$n \rightarrow \sigma^*$	Far-ultraviolet, sometimes near-ultraviolet	Acetone at 190 nm; methylamine at 213 nm
$\pi \rightarrow \pi^*$	Ultraviolet	Saturated aldehydes at 180 nm
$n \rightarrow \pi^*$	Near-ultraviolet and visible	Acetone at 277 nm; nitroso-t-butane at 665 nm

 $\boldsymbol{\epsilon}$ is a function of

- 1. Cross sectional area of absorbing species (Θ)
- 2. Transition probability (P)

 ϵ = 9X10¹⁹ Θ P (Θ = 10⁻¹⁵ cm²) = about 10⁵ for the average organic molecule



Transition Multiplicity

Consider two electrons paired in an orbital, and their possible transitions to an empty orbital.



- the ground state has all electrons in the lowest energyorbital
- organic compounds almost always have paired spins, thus their ground state is almost always a singlet
- singlet-triplet transitions are optically forbidden light cannot both promote an electron to a new orbital and change its spin
- in an organic compound most absorption spectra are due to singlet-singlet electronic transitions

Chromophores

 They are groups with one element of unsaturation (unsaturated linkages or groups) and cause coloring to the molecules when they are attached to a non-absorbing hydrocarbon chain

Effect of Multichromophores on Absorption

	-C≡C-	175	6000
 More chromophores in the same molecule cause bathochromic effect 	C=0	188	900
(Red shift: shift to longer wavelength)	/		
and hyperchromic effect (increase in	-NH ₂	195	2500
intensity)	-CHO	210	20
 Hypsochromic effect: Blue shift: shift to 	-COOR	205	50
shorter wavelengths	-COOH	205	60
Hypochromic effect: decrease in intensity	-N=N-	252	8000
• In the conjugated chromophores π^* electron	5	371	14
are delocalized over larger number of atoms	-N=0	300	100
causing a decrease in the energy of π to π^*		665	20
transitions and an increase in ϵ due to an	$-NO_2$	270	14
increase in probability for transition	—Br	205	400

TABLE 7.4. Representative

Approximate λ_{max} and ϵ_{max} Values

 λ_{max} , nm

185

€max

8000

Chromophores and Their

Chromophore



Auxochromes

- They are groups that do not confer color but increase the coloring power of a chromophore.
- They are functional groups that have non-bonded valence electrons and show no absorption at λ > 220 nm; they absorb in the far UV
- -OH and -NH₂ groups cause a red shift

Effect of polar solvents on transitions



Figure 6.12 Energy differences between *n* and π^* levels increase in solvents that can provide H to the lone pair. The absorption wavelength decreases (blue shift).



Figure 6.13 Expected absorption spectrum of a molecule undergoing $\pi \to \pi^*$ and $n \to \pi^*$ transitions. Note the different degrees of absorption in a nonpolar solvent.



Figure 6.11 The energy difference between π and π^* levels is decreased in the polar slovent; the absorption wavelength increases. This is the red shift.



Figure 6.13 Expected absorption spectrum of a molecule undergoing $\pi \to \pi^*$ and $n \to \pi^*$ transitions. Note the different degrees of absorption in a nonpolar solvent.

Electronic Transitions in Ethylene

- Attention will be restricted to electrons involved with carbon-carbon bonding
- The two sp² electrons form the σ -bond, while the two p_z electrons form the π -bond
- Absorption of a photon will promote one of the bonding electrons into an antibonding orbital, preserving electron spin
- The wavelength of absorbed light will follow
- Planck's Law, $E = hc/\lambda$
- The transition energies are: $\sigma \rightarrow \sigma^* > \sigma \rightarrow \pi^*, \ \pi \rightarrow \sigma^* > \pi \rightarrow \pi^*$
- The $\pi \to \pi^*$ transitions are of most interest since they give us information about the conjugated double bond structure of a molecule

$\pi \rightarrow \pi^*$ Transitions in Butadiene

Unconjugated Alkene Conjugated Diene 200 250 λ_{max} Onjugated Triene





The calculated value of λ_{max} is found to be 453.3 nm. and ε_{max} 19.1 × 10⁴.



- Each carbon atom has one electron in a p_z-orbital
- The four p_z electrons create two bonding π -orbitals and two anti-bonding π^* -orbitals
- $\pi_2 \to {\pi_2}^*$ absorption is in the deep UV, it has an energy similar to that in ethylene
- The longest wavelength absorption is due to the $\pi_1 \rightarrow {\pi_1}^*$ transition
- intermediate wavelength absorption is due to $\underline{\uparrow}_{\pi_2} \rightarrow \pi_1^*$ and $\pi_1 \rightarrow \pi_2^*$ transitions p_z • The long wavelength transition has an
- The long wavelength transition has an energy that decreases with the number of double bonds



p,

∕tJ

 \mathbf{p}_{z}

Biphenyls λ_{max} 270 (B-and)

 λ_{max} 254 (B-band)

Conjugation is greatest when the interacting functions allow maximum overlap of their π -orbitals system.

In biphenyls this would be achieved if the two benzene rings are coplanar.

Due to sterric reasons the two benzene rings are not coplanar, the average angle between the two benzene rings is 45°

58

Substituted Biphenyls CH3 ÇH₃ H₃C CH3 CH₃ H₂C H₂C CH λ_{max} 266 (B-band) ĊH

 λ_{max} 266 (B-band)

Bulky groups at ortho-positions of biphenyl molecules,

serves to increase the angle.

Effective conjugation is further reduced.

Due to sterric reasons the two benzene rings are orthogonal, no overlapping between the two rings.₅₉

α , β -unsaturated carbonyl compounds



Fig. 2.22. UV transitions in α , β -unsaturated corbonyl compounds.

Fig. 2.24. UVAbsorption spectra for conjugated and unconjugated carbonyl compounds.

There is hyperchromic shift also as the participating orbitals are extended over a larger area (i.e. 4atoms) than in C=O alone (i.e. 2 atoms only). We know ε increases with cross-sectional area of the bonding orbitals involved in the chromophore. This also applies in case of C=C conjugation also.





Charge Transfer Complexes



Fig. 2.29. Electronic transitions for charge-transfer complexes. Donor and acceptor orbitals combine to form two new orbitals (A and B) for the complex. New electronic transitions for long λ are then possible between A and B.



- The formation of charge-transfer complex occurs between molecules which, when mixed, allow the transfer of electronic charge through space from an electron rich molecule to an electron deficient molecule with molecular orbitals of suitable energy and symmetry.
- > The filled π -orbitals in the donor molecule overlap with the depleted orbital in the acceptor molecule and generate two new molecular orbitals. Thus transition between these newly formed orbitals are responsible for the new absorption bands observed in the charge transfer complexes.



When white light passes through or is reflected by a coloured substance,

a portion of the mixed wavelengths is absorbed.

The remaining light will then assume the complementary colour. Complementary colours are diametrically opposite each other. Absorption of 420-430 nm light renders a substance yellow, Absorption of 500-520 nm light makes it red.

Green is created by absorption of light close to 400 nm as well as absorption near 800 nm. 53

WOODWARD-FIESER RULES FOR CALCULATION OF ABSORPTION MAXIMA OF ORGANIC MOLECULES

As we know that the presence of auxochrome or extension of chromophore may cause the change in wavelength and the intensity of the absorption maximum. Woodward and Fieser formulated a set of empirical rules, which could be used to predict absorption maxima of conjugated systems like dienes, enones, aromatic systems (benzene and its derivatives), benzoyl compounds etc.

In 1945 Robert Burns Woodward gave certain rules for correlating λ_{max} with molecular structure.

In 1959 Louis Frederick Fieser modified these rules with more experimental data, and the modified rule is known as Woodward-Feiser Rules. It is used to calculate the position and λ_{max} for a given structure by relating the type of chromophores present, the substituents on the chromophores, and shifts due to the solvent.

According to Woodward's rules the λ_{max} of the molecule can be calculated using a formula:

 $\lambda_{max} = Base \ value + \Sigma \ Substituent \ Contributions + \Sigma \ Other \ Contributions$

Woodward-Fieser Rule for conjugated dienes or polyenes

Table T2-8. Conjugated dienes and Trienes.Solvent-EthanolTransition involved— $\pi \to \pi^*$		
conjugated diene	→217 mµ	
Acyclic Triene	245 mµ	
Homoannular conjugated diene	—→ 253 mµ	
Heteroannular conjugated diene	<u>→215</u> mµ	
Increment for each substituent	214	
Alkyl substituent or ring residue	>5 mµ	
Exocyclic double bond		
Double bond extending conjugation		
Auxochrome	(b) Hoinepannular co	
—OR	+ 6 mµ	
for $-SR$ and to transmission polynomials when	+ 30 mµ	
Cl*,Br*	+ 5 mµ	
-NR ₂	+ 60 mµ	
OCOCH ₃	0 mµ	

(CH₃-CH=CH-CH=CH-CH₃) Basic value = 217 mµ 2-alkyl substituents $(2 \times 5) = 10 \text{ m}\mu$ Calculated value = $\overline{227 \text{ m}\mu}$ The observed value** is also found to be 227 mu.

> $C - CH = CH + CH_3$ CH₃

Sidues on the double com The value of absorption maximum is calculated as follows : = 217 mµ Basic value 2-alkyl substituents $(2 \times 5) = 10 \text{ m}\mu$ 2-Ring residues (2×5) = 10 mµ 1-Exocyclic double bond = $5 \text{ m}\mu$ $= 242 \, m\mu$ Calculated value The observed value is also found to be 242 mµ.



214 =-215 mμ Basic value Four Ring residues $(4 \times 5) = 20 \ \mu m$ $= 235 \text{ m}\mu$ Calculated value The observed value is also found to be 234 mµ,.

C-



Basic value 3-Ring residues (3 × 5) 1-exocyclic double bond Calculated value Observed value

- Basic value 3-Ring residues 1-exocyclic double bond Calculated value



= 253 mµ

= 15 mµ

 $= 5 \text{ m}\mu$

= 273 mµ

= 274 mµ



Basic value	= 253 mµ
2-double bonds extending conjugation	$2 \times 30 = 60 \text{ m}\mu$
5-Ring residues	$5 \times 5 = 25 \text{ m}\mu$
1-Exocyclic double bond	$1 \times 5 = 5 \text{ m}\mu$
Calculated value	$=$ 343 m μ
Observed value	= 345 mµ

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	\sim
Basic value	
4-Ring residues	(4 ×

Dusic funde		
4-Ring residues	$(4 \times 5) =$	20 mµ
2-exocyclic double bonds	$(2 \times 5) =$	10 mµ
1-double bond extending conjugation		30 mµ
Calculated value	=	313 mµ
Observed value	€Y.109 (¥	312 mµ

= 253 mµ

Basic value		217 mµ
2-Ring residues	$(2 \times 5) =$	10 mµ
2-Exocyclic double bonds	~(TD=)을	10 mµ
I-bicyclic system (strain correction)	=	15 mµ
Calculated value	=	252 mµ
Observed value		254 mµ

		1
1,2-Dimethylenecyc	lohexane	
Parent	253 nm	217
chromophore		_
Ring residue	5X2=10	_
Exocyclic	5X2=10	-
double bonds		
Total	273 nm	237
$\lambda_{observed}$	220 nm	
Difference	53 nm	17



For polyenes with more than 4 conjugated double bonds, Fieser-Kuhn rule is used to calculate λ_{max}

Fieser-Kuhn derived the following equation to calculate the wavelength of maximum absorption λ_{max} and also maximum absorptivity ε_{max}

 $\lambda_{max} = 114 + 5x + y (48.0 - 1.7 y) - 16.5 R_{endo} - 10 R_{exo}$ Where,

- λ_{max} = wavelength of maximum absorption
- x = number of alkyl substituents / ring residues in the conjugated system
- y = number of conjugated double bonds
- **R**_{endo}= number of rings with endocyclic double bonds in the conjugated system
- **R**_{exo} = number of rings with exocyclic double bonds in the conjugated system

$\varepsilon_{\rm max} = (1.74 \ {\rm x} \ 10^4) \ {\rm y}$

Where,

 ε_{max} = maximum absorptivity

 $\mathbf{y} =$ number of conjugated double bonds

Let us take β -carotene as an example. The observed λ_{max} of β carotene is 452 nm, while the observed ε_{max} is 15.2 x 10⁴.



x (number of alkyl substituents) = 10 y (number of conjugated double bonds) = 11 R_{endo} (number of endocyclic double bonds) = 2 R_{exo} (number of exocyclic double bonds) = 0

Thus
$$\lambda_{max} = 114 + 5x + y (48.0 - 1.7 y) - 16.5 R_{endo} - 10 R_{exo}$$

= 114 + 5(10) + 11 (48.0 - 1.7(11)) - 16.5 (2) - 10 (0)
= 114 + 50 + 11 (29.3) - 33 - 0
= 114 + 50 + 322.3 - 33
= 453.30 nm

 $\varepsilon_{\text{max}} = (1.74 \text{ x } 10^4) \text{ y}$ = (1.74 x 10⁴) 11 = 19.14 x 10⁴

Woodward-Fieser Rule for α,β-unsaturated carbonyl compounds

Base value for

- a) Acyclic α , β unsaturated ketones = 215 nm
- b) 6 membered cyclic α , β unsaturated ketones = 215 nm
- c) 5 membered cyclic α , β unsaturated ketones = 202 nm
- d) α , β unsaturated aldehydes = 210 nm
- e) α , β unsaturated carboxylic acids and esters = 195 nm

Increment for

- ii) Each double bond extending conjugation = 30 nm
- iii) Exocyclic double bonds = 5 nm
- iv) Homoannular diene component = 39 nm

Increment for substituents

Substituents	a position	β position	γ position	δ position
Each alkyl substituent or Ring residue	10 nm	12 nm	18 nm	18 nm
-OH	35 nm	30 nm	50 nm	50 nm
-OAc	6 nm	6 nm	6 nm	6 nm
-OMe	35 nm	30 nm	17 nm	31 nm
-Cl	15 nm	12 nm	12 nm	12 nm
-Br	25 nm	30 nm	25 nm	25 nm
-SR	-	85 nm	-	-
-NR ₂	-	95 nm	-	-

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CH ₃ O	Srena di 1905
CH_{1} $C=CH-C-C$ Basic value	= 215 mu
2β -alkyl substituents (2×12)	$= 24 \text{ m}\mu$
Calculated value	= 239 mµ.



Basic value = $215 \text{ m}\mu$ 2β -ring residues $(2 \times 12) = 24 \text{ m}\mu$ $1 \text{ exocyclic double bond} = <math>5 \text{ m}\mu$ Calculated value = $244 \text{ m}\mu$ The observed value is found to be 241 m μ .



Basic value = $215 \text{ m}\mu$

OH substitution at α - position = 35 mµ 2 β -substituents (one alkyl) and one ring residue) = 24 mµCalculated value = 274 mµObserved value = 275 mµ





Basic value	= 215 mµ
1 β-ring residue	= 12 mµ
1 (δ + 1) ring residue	= 18 mµ
2 (δ + 2) ring residues	= 36 mµ
(2 × 18)	4.2.10 at 14.17
2 double bonds	a he selle as
extending conjugation	
(2 × 30)	$= 60 \text{ m}\mu$
2 exocyclic double	Section Land Land
bonds (2×5)	$= 10 \text{ m}\mu$
Calculated value	= 351 mµ
Observed value	= 354 mµ

b) Calculate the λ_{max} values for the following. Use the table provided in the appendix.



α-ring residue	=	10 mµ
δ-ring residue	=	18 mµ
1 exocyclic double bond	n =	5 mµ
Homoannular conjugated		
diene	=	39 mµ
1 double bond extending		
conjugation		30 mµ
Calculated value	0=	317 mµ
Observed value	=	319 mµ

Woodward-Fieser Rule for benzene and its derivatives

- 1) Base values for
- a) ArCOR = 246 nm
- b) ArCHO = 250 nm
- c) $ArCO_2H = 230 \text{ nm}$
- d) $ArCO_2R = 230 \text{ nm}$

2) Increment for substituents:

Substituents	ortho	meta	Para
Alkyl group or ring residue	3 nm	3 nm	10 nm
–OH, –OCH ₃ , –OAlkyl	7 nm	7 nm	25 nm
-O (oxonium)	11 nm	20 nm	78 nm
-Cl	0 nm	0 nm	10 nm
-Br	2 nm	2 nm	15 nm 🔊
-NH ₂	13 nm	13 nm	58 nm
-NHCOCH ₃	20 nm	20 nm	45 nm
-NHCH ₃	514	de -	73 nm
-N(CH ₃) ₂	20 nm	20 nm	85 nm



Basic value	= 246 mµ
Cl-substitution at	r aro na printa di data di
para position	$= 10 \text{ m}\mu$
Calculated value	= 256 mµ
The observed value	is found to be 254 mµ.



Basic value	1	246	mμ
OH substitution at meta) (11) (12)	7	mμ
OH substitution at para	-	25	mμ
Calculated value	=	278	mμ
Observed value	=	281	mμ



Br

Basic value	i sitte	230 mµ
Br substitution at para	::i≞	15 mµ
Calculated value	5.1	245 mµ
Observed value	Ga <u>n</u>	245 mu