Ultra-Violet / Visible Spectroscopy- Section 4

Electron Transition for Ethylene with a Substitute Possessing Lone Pair

- Hyper-conjugation:
- ✓ extension of π system by resonance effect of lone pair
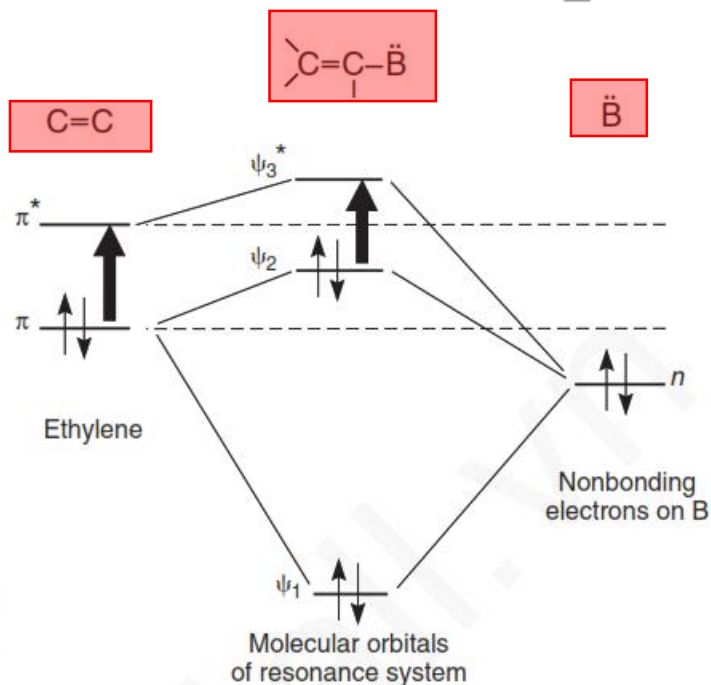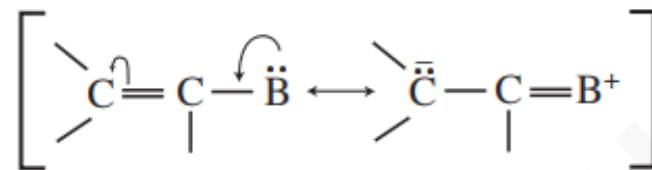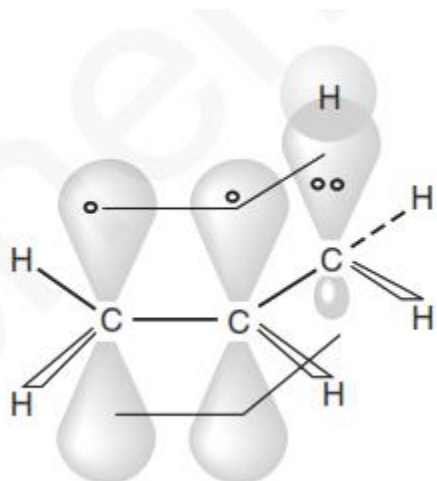- ✓ decrease conjugation due to inductive effect of heteroatom

FIGURE 7.14 Energy relationships of the new molecular orbitals and the interacting π system and its auxochrome.

Functional Groups as Chromophores

- Compare λ_{max} & ϵ in different functional groups due to the type of electron transition levels.

TABLE 7.3
TYPICAL ABSORPTIONS OF SIMPLE ISOLATED CHROMOPHORES

Class	Transition	λ_{max} (nm)	log ε	Class	Transition	λ_{max} (nm)	log ε
$R-OH$	$n \rightarrow \sigma^*$	180	2.5	$R-NO_2$	$n \rightarrow \pi^*$	271	<1.0
$R-O-R$	$n \rightarrow \sigma^*$	180	3.5	$R-CHO$	$\pi \rightarrow \pi^*$	190	2.0
$R-NH_2$	$n \rightarrow \sigma^*$	190	3.5		$n \rightarrow \pi^*$	290	1.0
$R-SH$	$n \rightarrow \sigma^*$	210	3.0	R_2CO	$\pi \rightarrow \pi^*$	180	3.0
$R_2C=CR_2$	$\pi \rightarrow \pi^*$	175	3.0		$n \rightarrow \pi^*$	280	1.5
$R-C\equiv C-R$	$\pi \rightarrow \pi^*$	170	3.0	$RCOOH$	$n \rightarrow \pi^*$	205	1.5
$R-C\equiv N$	$n \rightarrow \pi^*$	160	<1.0	$RCOOR'$	$n \rightarrow \pi^*$	205	1.5
$R-N=N-R$	$n \rightarrow \pi^*$	340	<1.0	$RCONH_2$	$n \rightarrow \pi^*$	210	1.5

Electron Transitions for Un-Saturated Functional Group Possessing Oxygen or Nitrogen

- Carbonyl (C=O) or imine (C=N):
- Electron transitions:
- ✓ π-π*transition: λ_{max}= 190nm
- ✓ n-π* transition: λ_{max}=280-290nm

Є = 15

CARBONYL COMPOUNDS; ENONES
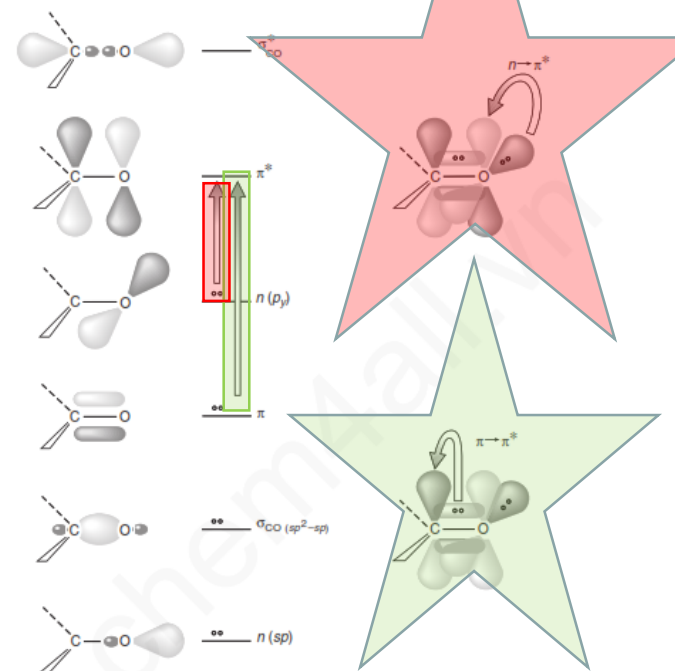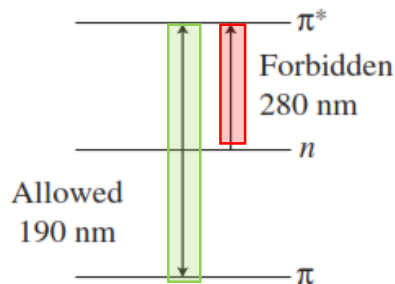
FIGURE 7.9 Electronic transitions of the carbonyl group.

π*
Forbidden
280 nm
n
Allowed
190 nm
π

Table 7.3 lists typical absorptions of simple isolated chromophores. You may notice that these *simple* chromophores nearly all absorb at approximately the same wavelength (160 to 210 nm).

The attachment of substituent groups in place of hydrogen on a basic chromophore structure changes the position and intensity of an absorption band of the chromophore. The substituent groups may not give rise to the absorption of the ultraviolet radiation themselves, but their presence modifies the absorption of the principal chromophore. Substituents that increase the intensity of the absorption, and possibly the wavelength, are called **auxochromes.** Typical auxochromes include methyl, hydroxyl, alkoxy, halogen, and amino groups.

Other substituents may have any of four kinds of effects on the absorption:

- Describe the changes if a carbon or heteroatom is attached to carbonyl group.

4

Effect of Auxochromes on Maximum Absorption Wavelengths of Carbonyls

- Consider angle of methyl to carbonyl in sp^2 hybridization to discuss shorter λ

- Lone pair of auxochrome has:

✓ bathochromic effect on π - π*

✓ hypsochromic effect on n - π*

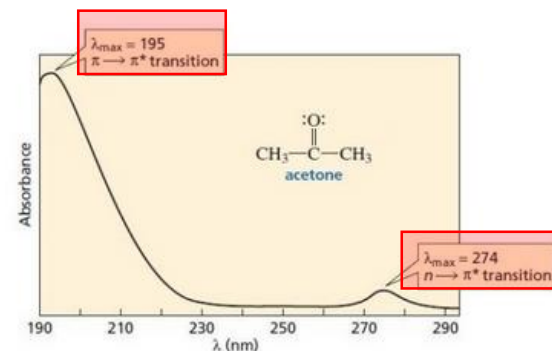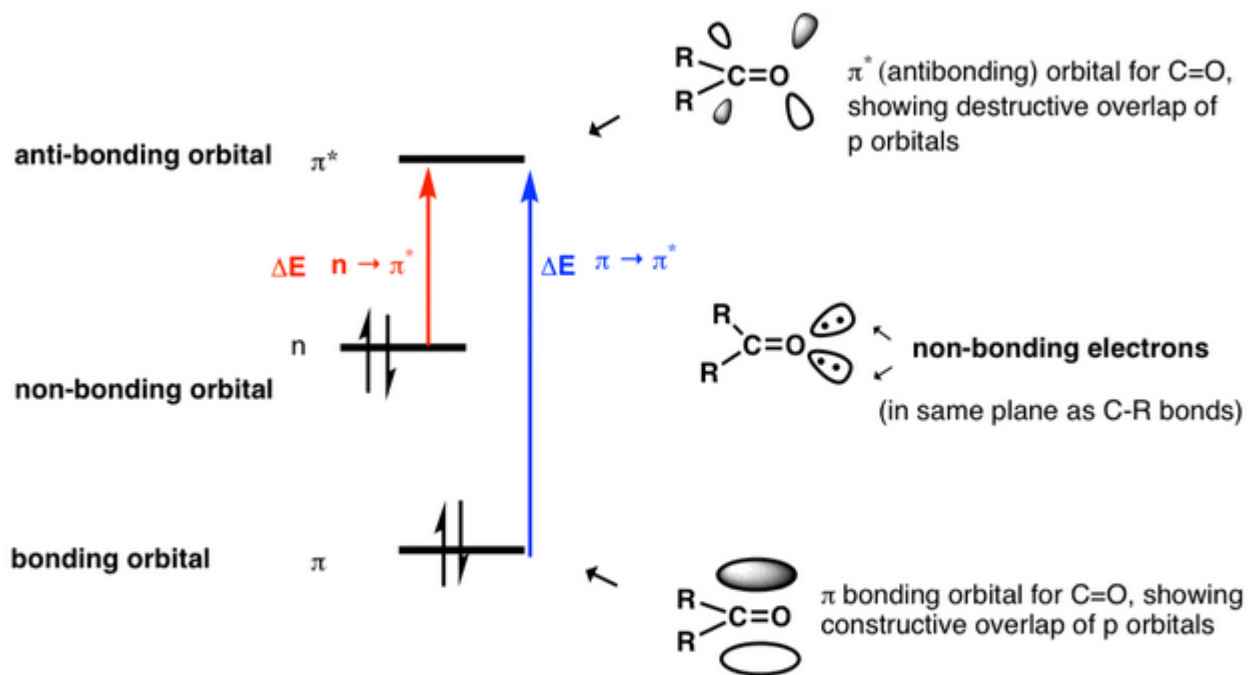- Also consider solvent effect:

✓ solvation of base state comparing to

✓ solvation of excited state

TABLE 7.6

HYPSOCHROMIC EFFECTS OF LONE-PAIR AUXOCHROMES ON THE n → π* TRANSITION OF A CARBONYL GROUP

	λ_{max}	ε_{max}	Solvent
$CH_3-\overset{O}{\overset{\|\|}{C}}-H$	293 nm	12	Hexane
$CH_3-\overset{O}{\overset{\|\|}{C}}-CH_3$	279	15	Hexane
$CH_3-\overset{O}{\overset{\|\|}{C}}-Cl$	235	53	Hexane
$CH_3-\overset{O}{\overset{\|\|}{C}}-NH_2$	214	—	Water
$CH_3-\overset{O}{\overset{\|\|}{C}}-OCH_2CH_3$	204	60	Water
$CH_3-\overset{O}{\overset{\|\|}{C}}-OH$	204	41	Ethanol

UV Characteristics for Acetone as a Ketone

Simplified Molecular Orbital Diagram for Acetone (Propanone)

anti-bonding orbital π^*

π^* (antibonding) orbital for C=O, showing destructive overlap of p orbitals

ΔE $n \rightarrow \pi^*$ ΔE $\pi \rightarrow \pi^*$

non-bonding orbital n

non-bonding electrons

(in same plane as C-R bonds)

bonding orbital π

π bonding orbital for C=O, showing constructive overlap of p orbitals

$\lambda_{max} = 195$
$\pi \rightarrow \pi^*$ transition

$\lambda_{max} = 274$
$n \rightarrow \pi^*$ transition

Absorbance

190   210   230   250   270   290
λ (nm)

:O:
CH_3-C-CH_3
acetone

· Electrons in the non-bonding orbital (n) are higher-energy than electrons in the bonding π orbital

· The transition from the non-bonding orbital (n) to the empty π^* orbital requires less energy (ΔE) than the transition from the bonding π orbital to the empty π^* orbital (ΔE)

· The absorption maximum (λ_{max}) at 275 nm corresponds to the $n \rightarrow \pi^*$ transition

· The absorption maximum (λ_{max}) for the $\pi \rightarrow \pi^*$ transition is at about 190 nm

UV Spectra for a Couple of Conjugated Aldehydes

- Bathochromic & hyperchromic on π-π* & n-π*transitions
- However, changes are more intense on π - π*
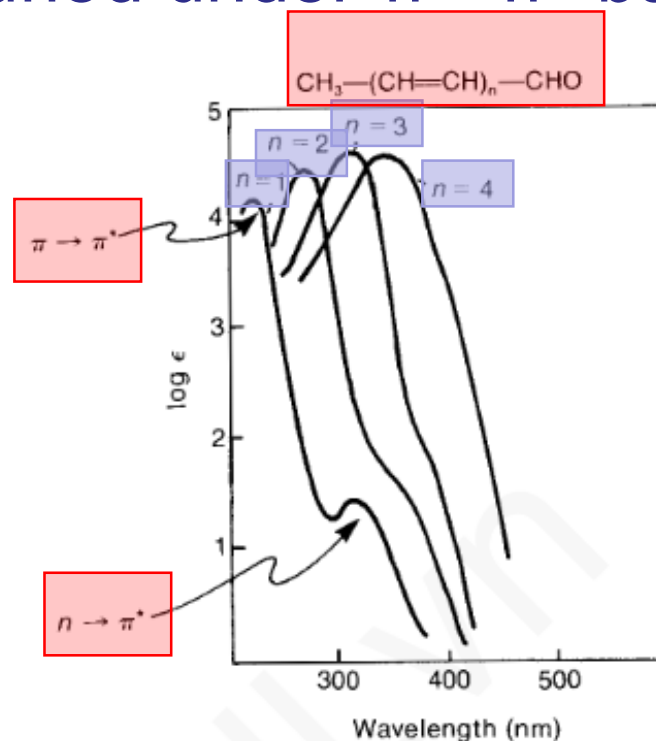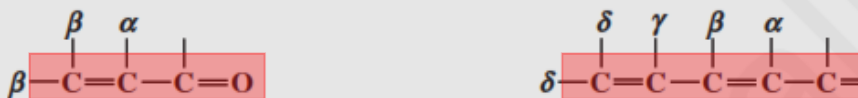- Hence, n - π* bands are buried under π - π* bands

FIGURE 7.15 The spectra of a series of polyene aldehydes. (From Murrell, J. N., *The Theory of the Electronic Spectra of Organic Molecules*, Methuen and Co., Ltd., London, 1963. Reprinted by permission.)

Woodward-Fieser Rules to Calculate Theoretical Maximum Absorption Wavelength of Conjugated Carbonyls or enones

TABLE 7.7
EMPIRICAL RULES FOR ENONES

$$\overset{\beta}{\beta}-\overset{}{C}=\overset{\alpha}{C}-\overset{}{C}=\overset{}{O} \qquad \overset{\delta}{\delta}-\overset{}{C}=\overset{\gamma}{C}-\overset{\beta}{C}=\overset{\alpha}{C}-\overset{}{C}=$$

Base values:	
Six-membered ring or acyclic parent enone	= 215 nm
Five-membered ring parent enone	= 202 nm
Acyclic dienone	= 245 nm
Increments for:	
Double-bond-extending conjugation	30
Alkyl group or ring residue	α 10
	β 12
	γ and higher 18
Polar groupings:	
—OH	α 35
	β 30
	δ 50
—OCOCH$_3$	α,β,δ 6
—OCH$_3$	α 35
	β 30
	γ 17
	δ 31
—Cl	α 15
	β 12
—Br	α 25
	β 30
—NR$_2$	β 95
Exocyclic double bond	5
Homocyclic diene component	39
Solvent correction	Variable
λ_{max}^{EtOH}(calc) = Total	

Comparing Electron Transitions for Alkene, Carbonyl & Enone Systems

- Bathochromic effect in enone system:

310-330nm   320 nm

220-250nm   218 nm

165 nm

280 nm

190 nm

ψ_4^*

ψ_3^*

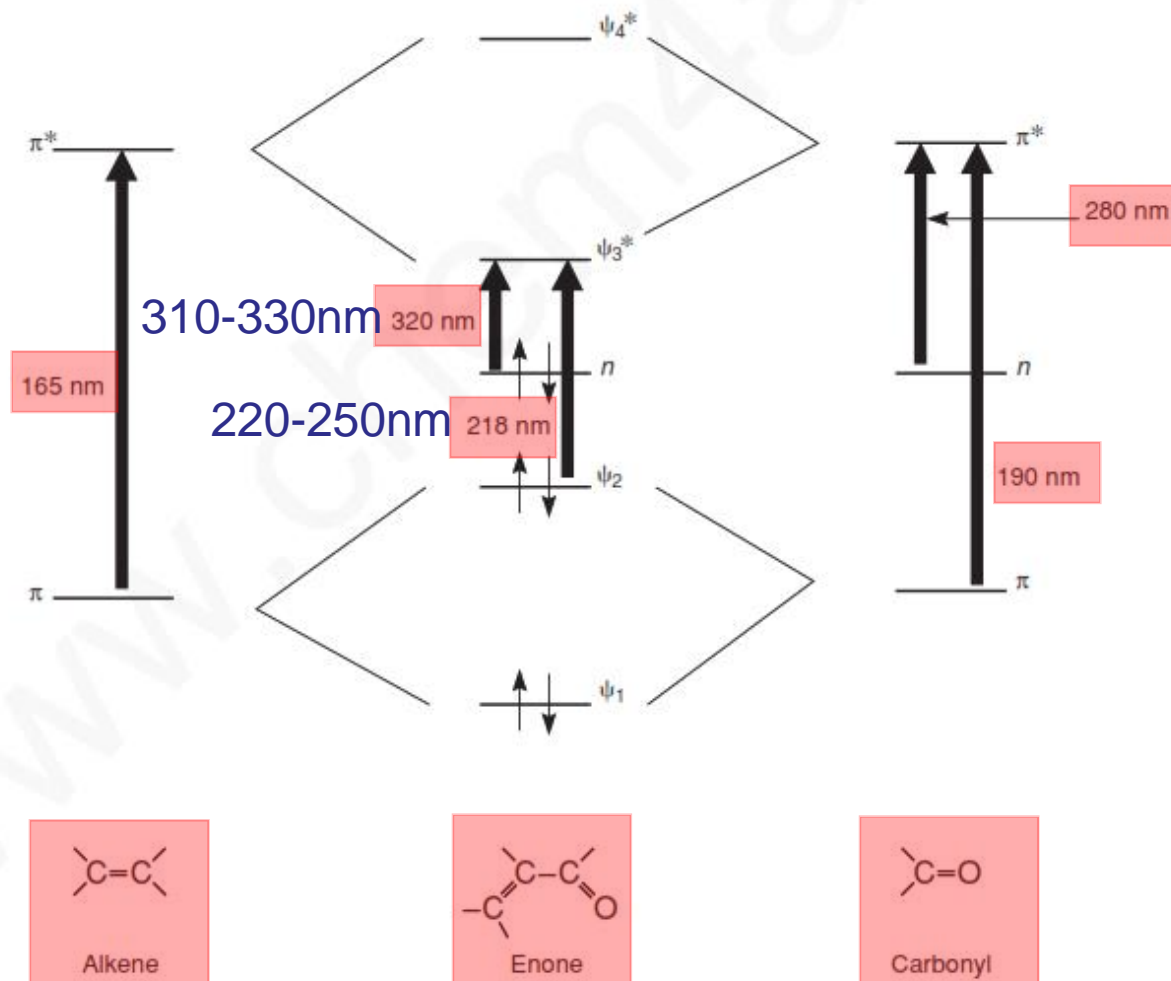ψ_2

ψ_1

π^*

π

n

Alkene

Enone

Carbonyl

FIGURE 7.16 The orbitals of an enone system compared to those of the noninteracting chromophores.

9

Solvent Effect on UV Spectrum and λ_{max}

- Compare energy state of base state after solvation of to excited state.

- Polar solvent including ability of hydrogen bond:

✓ stabilize π*

hence decrease E required for π-π* transition

bathochromic effect on λ_{max}

✓ stabilize n

hence increase E required for n-π* transition

hypsochromic effect on λ_{max}

Electron Transitions for Aromatics & Poly-Armoatics

π_6^*

π_4^* π_5^*

π_2 OO   OO π_3

π_1 OO

(a) Molecular orbitals

E_{1u}

180 nm (allowed)

B_{1u}

200 nm (forbidden)

B_{2u}

260 nm (forbidden)

A_{1g}
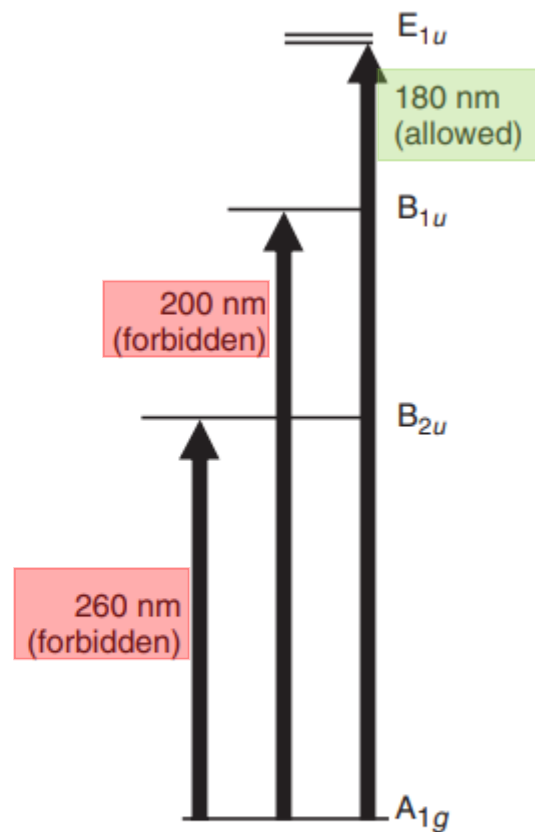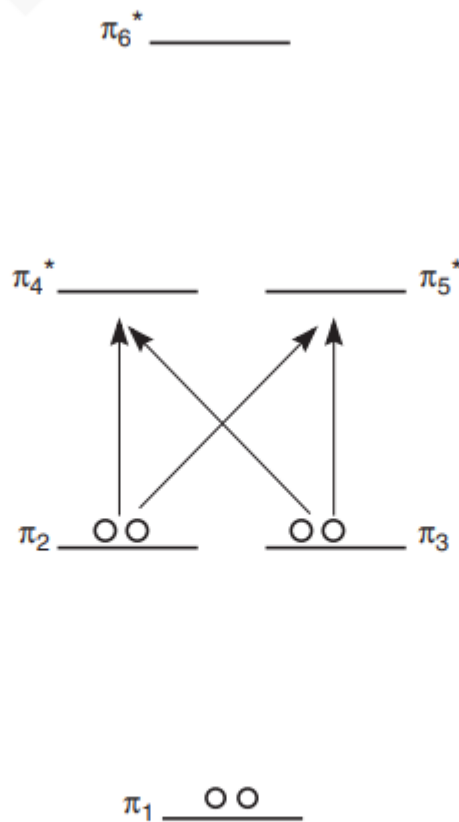
(b) Energy states

FIGURE 7.17 Molecular orbitals and energy states for benzene.

11

UC Spectrum for Benzene

- **Three electron transitions:**

✓ two primary transition:

one is allowed (180-184nm):ɛ=47000

& one is forbidden (200-202nm):ɛ=7400

✓ one secondary transition:

is forbidden (250-260nm):ɛ=204 -230

- **Substitute effect:** enables n-π*transition

✓ bathochromic & hyperchromic

- pH effect on substitutes
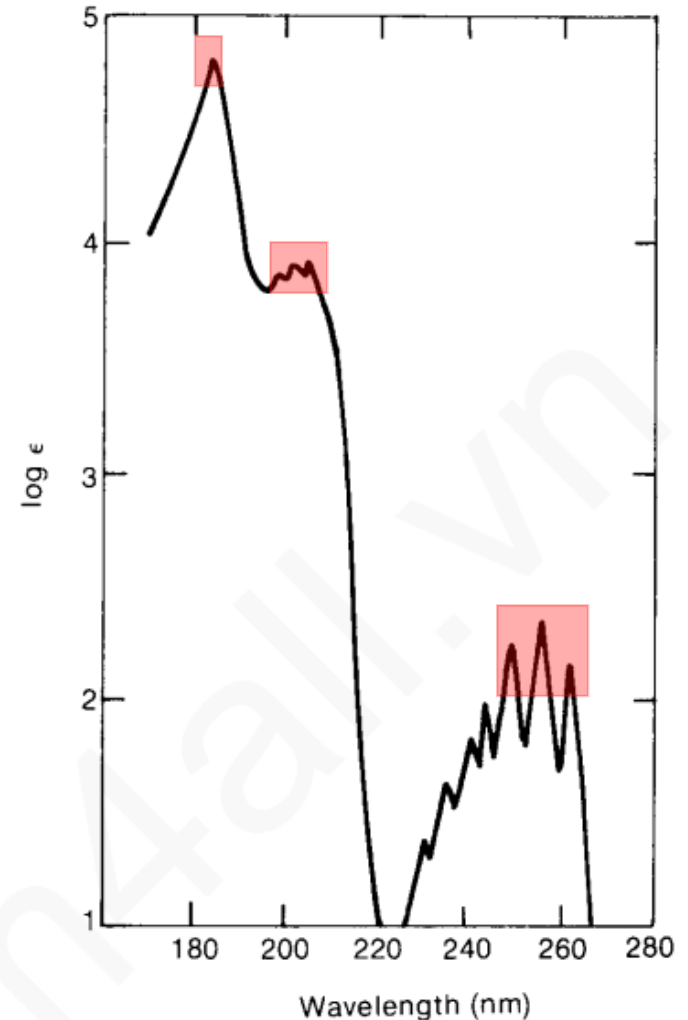
FIGURE 7.18 Ultraviolet spectrum of benzene.
(From Petruska, J., *Journal of Chemical Physics, 34*
(1961): 1121. Reprinted by permission.)

UV Spectrum for Polycyclic Aromatics
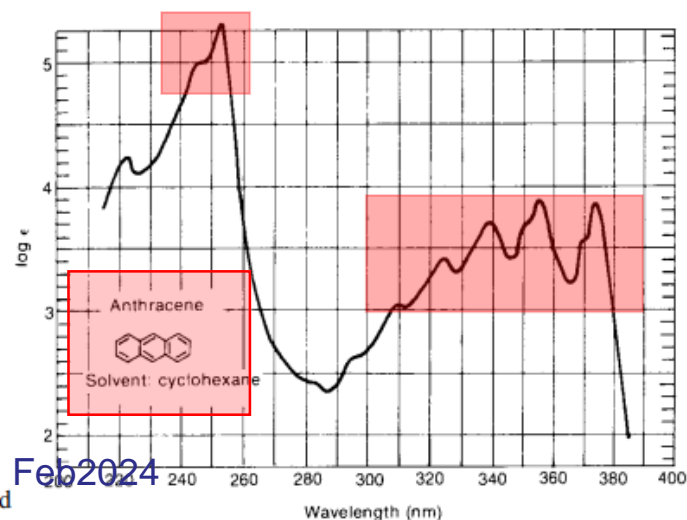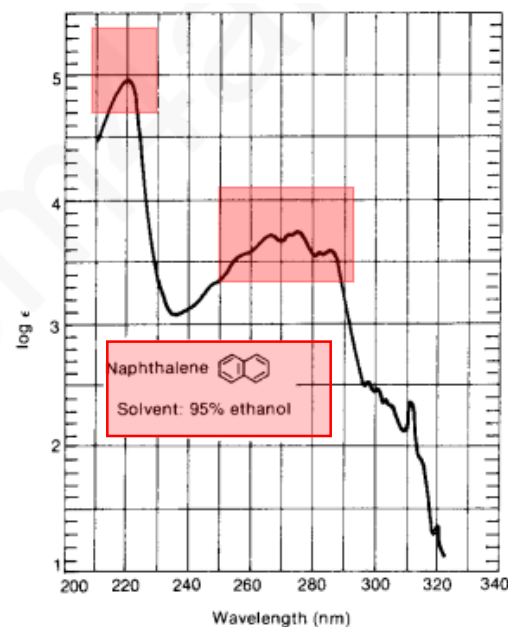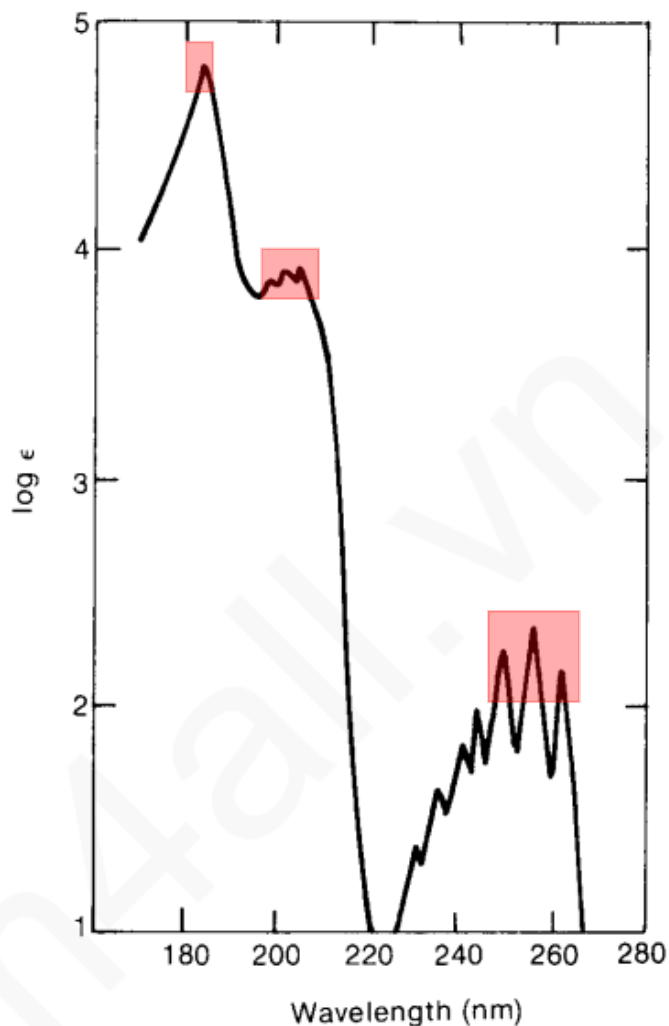
FIGURE 7.19 Ultraviolet spectra of naphthalene and anthracene. (From Friedel, R. A., and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley and Sons, New York, 1951. Reprinted by permission.)

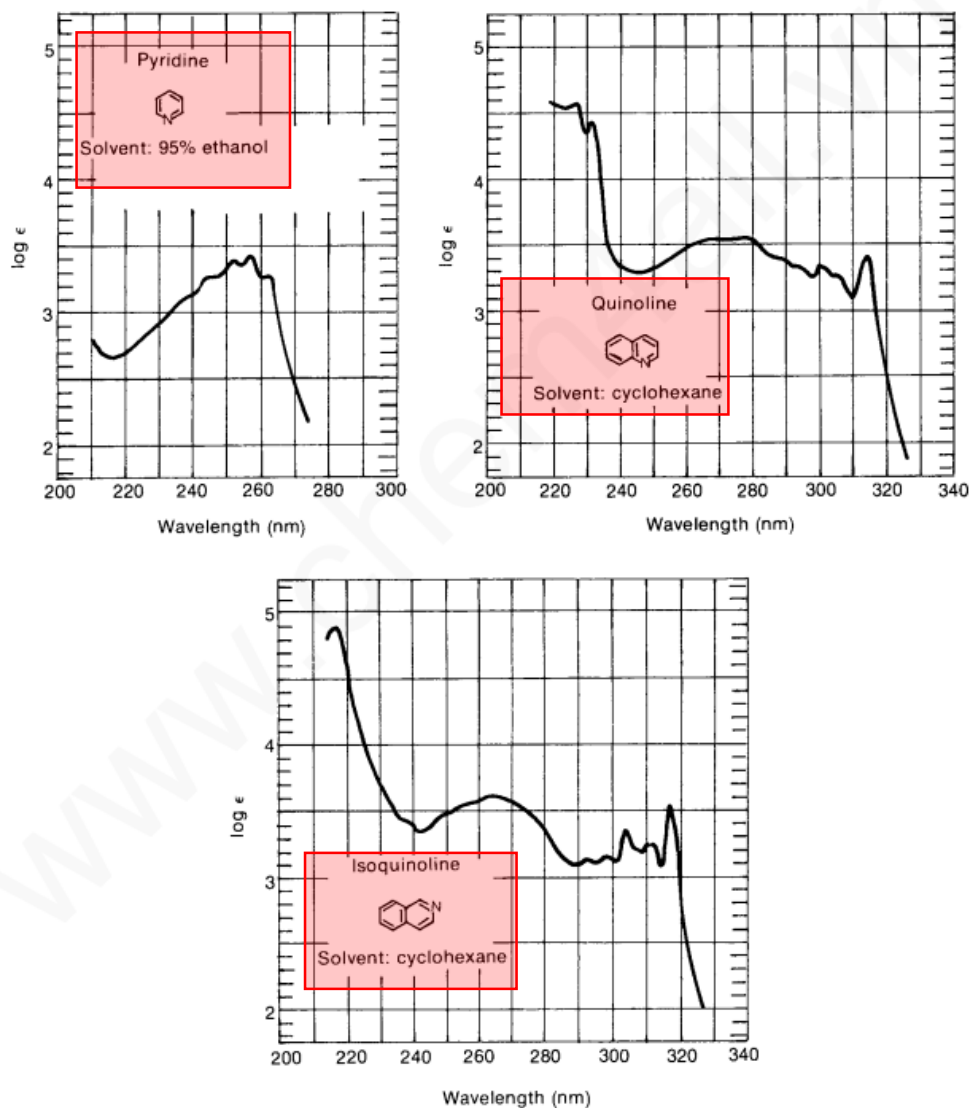# UV Spectrum for Hetero-Aromatics & Polycyclic Hetero-Aromatics
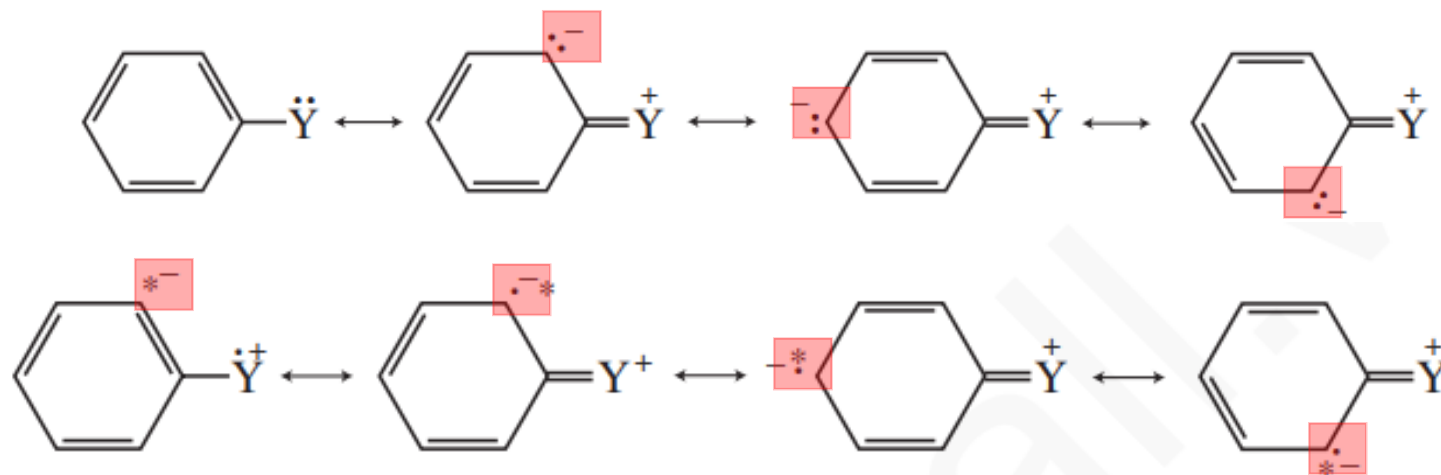

FIGURE 7.20 The ultraviolet spectra of pyridine, quinoline, and isoquinoline. (From Friedel, R. A., and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley and Sons, New York, 1951. Reprinted by permission.)

Effect of Resonance & Induction of Substitutes on Aromatics

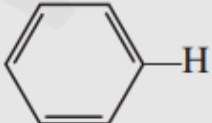- Lone pairs on substitutes: amine; hydroxy; alkoxy; X

- Electron donation or withdrawing by substitutes

- Conjugation by substitutes:
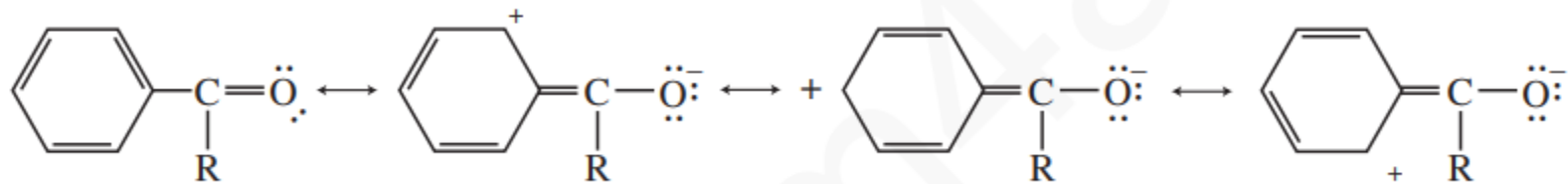
TABLE 7.10
pH EFFECTS ON ABSORPTION BANDS

Substituent	Primary		Secondary	
	λ (nm)	ε	λ (nm)	ε
—H	203.5	7,400	254	204
—OH	210.5	6,200	270	1,450
—O$^-$	235	9,400	287	2,600
—NH$_2$	230	8,600	280	1,430
—NH$_3^+$	203	7,500	254	169
—COOH	230	11,600	273	970
—COO$^-$	224	8,700	268	560

TABLE 7.11
ULTRAVIOLET MAXIMA F

Substituent	Primary		Secondary	
	λ (nm)	ε	λ (nm)	ε
—H	203.5	7,400	254	204
—CH₃	206.5	7,000	261	225
—Cl	209.5	7,400	263.5	190
—Br	210	7,900	261	192
—OH	210.5	6,200	270	1,450
—OCH₃	217	6,400	269	1,480
—NH₂	230	8,600	280	1,430
—CN	224	13,000	271	1,000
—COOH	230	11,600	273	970
—COCH₃	245.5	9,800		
—CHO	249.5	11,400		
—NO₂	268.5	7,800		

Electron-releasing substituents

Electron-withdrawing substituents

17

Woodward-Fieser Rules to Calculate Theoretical Maximum Absorption Wavelength for Benzoyl Derivatives

TABLE 7.12
EMPIRICAL RULES FOR BENZOYL DERIVATIVES
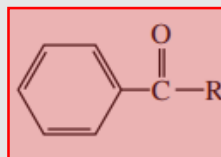

Parent chromophore:		
R = alkyl or ring residue		246
R = H		250
R = OH or Oalkyl		230
Increment for each substituent:		
—Alkyl or ring residue	*o, m*	3
	p	10
—OH, —OCH$_3$, or —Oalkyl	*o, m*	7
	p	25
—O$^-$	*o*	11
	m	20
	p	78
—Cl	*o, m*	0
	p	10
—Br	*o, m*	2
	p	15
—NH$_2$	*o, m*	13
	p	58
—NHCOCH$_3$	*o, m*	20
	p	45
—NHCH$_3$	*p*	73
—N(CH$_3$)$_2$	*o, m*	20
	p	85