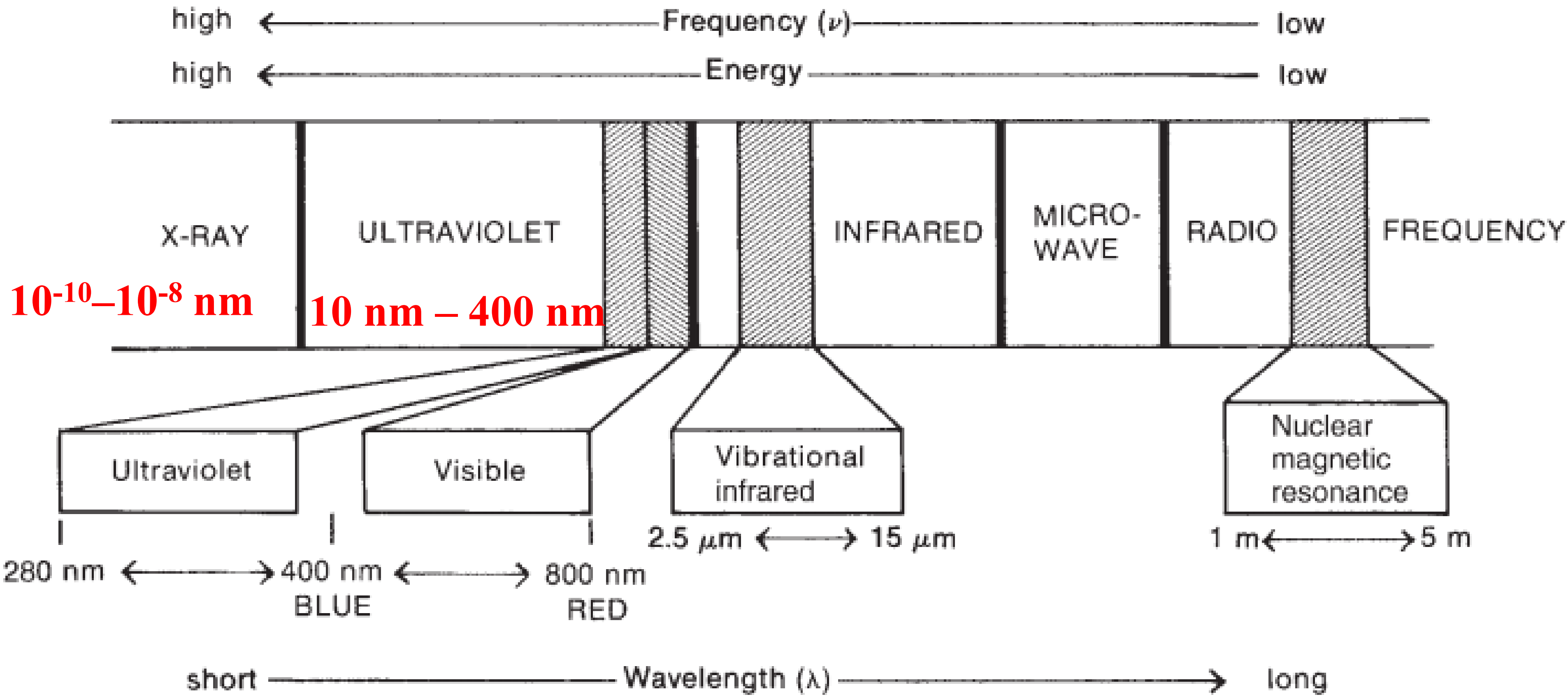
Chapter 6

Part III

UV-Vis Spectroscopy

THE ELECTROMAGNETIC RANGE



10^{-10}–10^{-8} nm

10 nm – 400 nm

THE NATURE OF ELECTRONIC EXCITATIONS

- When continuous radiation passes through a transparent material, a portion of the radiation may be absorbed.
- As a result of energy absorption, atoms or molecules pass from a state of low energy (the initial, or **ground state**) to a state of higher energy (the **excited state**).

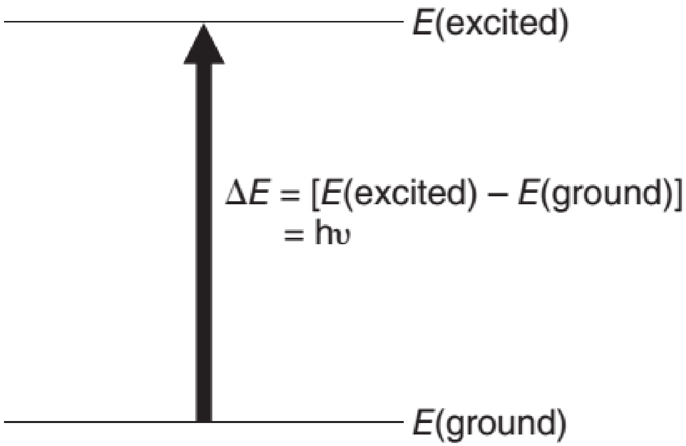


FIGURE 10.1 The excitation process.

- The electromagnetic radiation that is absorbed has energy exactly equal to the energy *difference* between the excited and ground states.

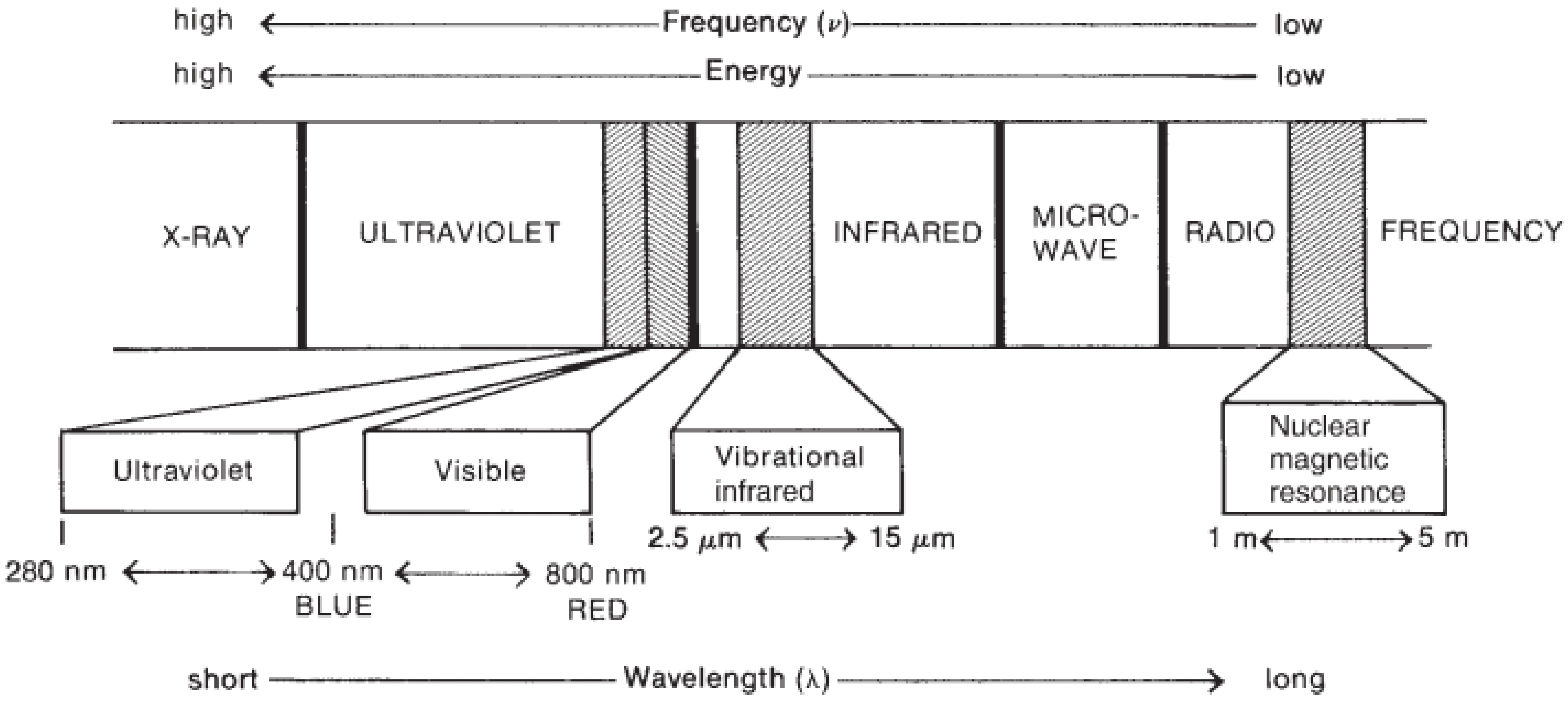
Types of spectroscopy

Electromagnetic range	Type of spectroscopy	Transition between	Used to determine
Infrared (2,5 – 15 μm) (400 - 4000 cm^{-1})	IR spectroscopy	Vibrational energy levels	Functional groups
Radio-wave (1 m – 5 m)	NMR spectroscopy	Nuclear spin states	Carbon–hydrogen framework
Ultraviolet (~ 200 – 400 nm) – Visible (~400-800 nm)	UV-Vis spectroscopy	Electronic energy levels	Nature and extent of conjugated π electron system

- **Mass spectroscopy** - Molecular size and formula

The UV-Vis region

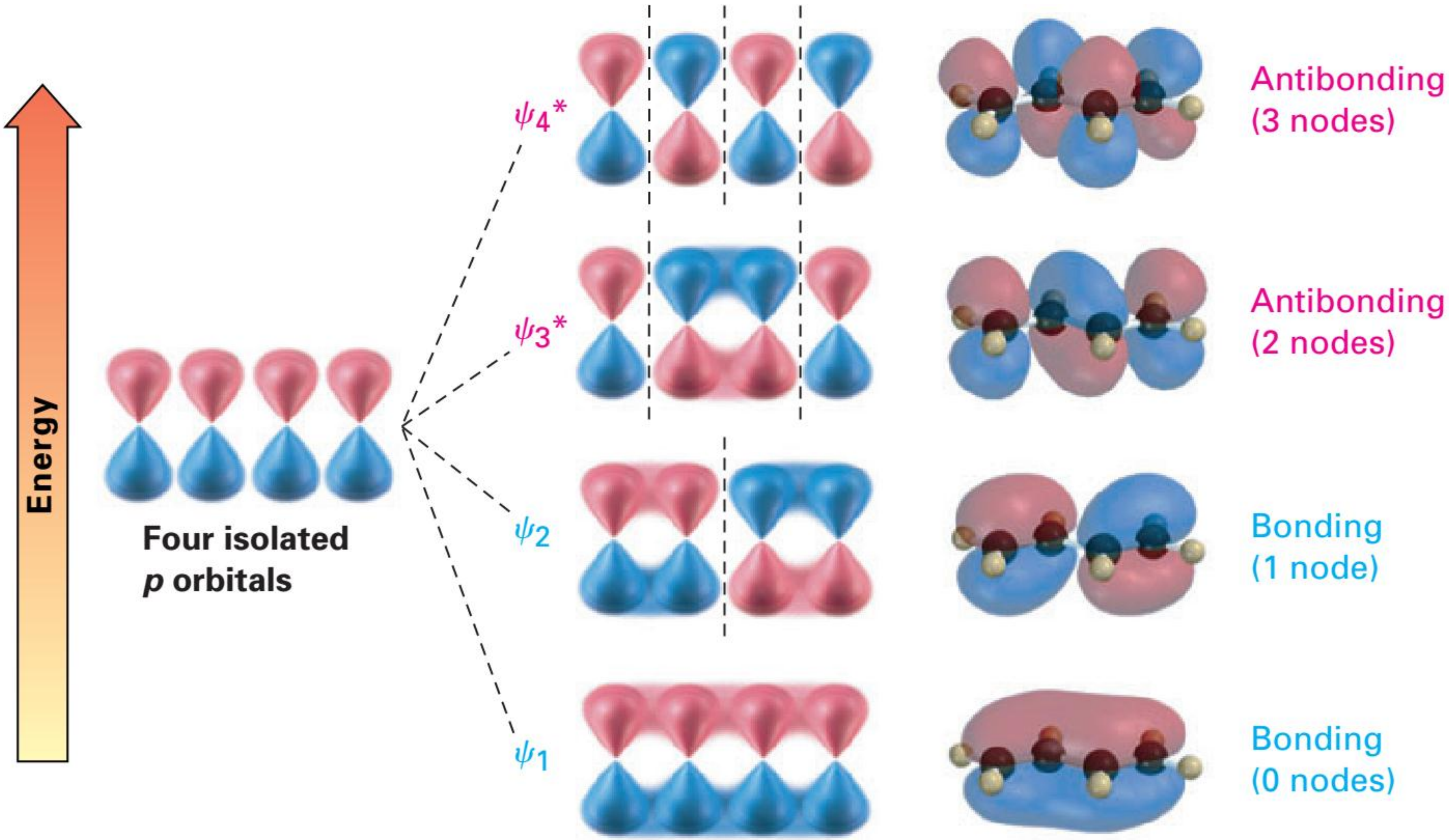
- The **ultraviolet** (UV) and **visible** (Vis) regions are the portions of the electro-magnetic spectrum where wavelengths range from 200 nm to 800 nm.

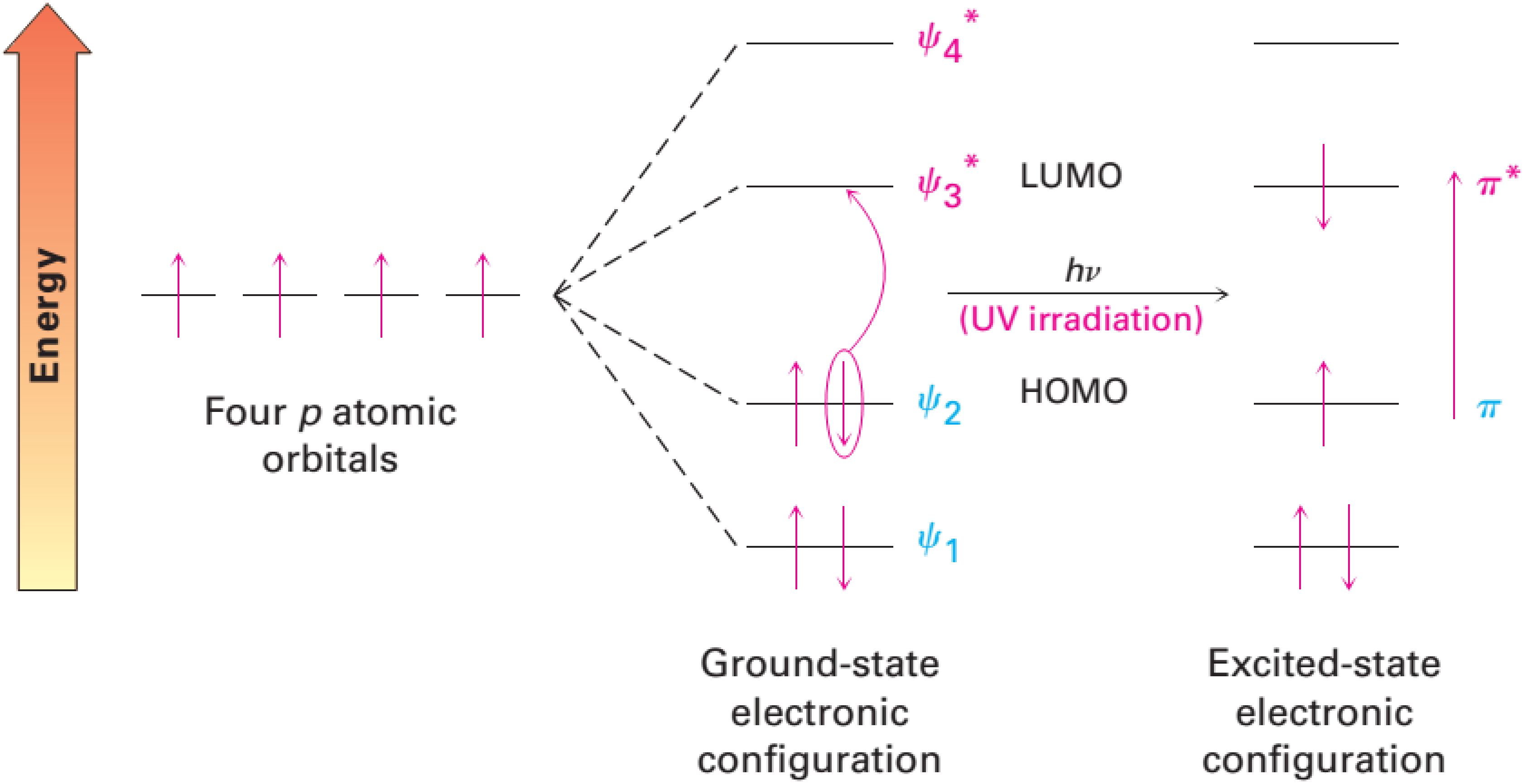


- In the case of **ultraviolet and visible** spectroscopy, the transitions that result in the absorption of electromagnetic radiation in this region of the spectrum are **transitions between electronic energy levels**.

- As a molecule absorbs energy, an electron is promoted from an occupied orbital to an unoccupied orbital of greater potential energy.

- Generally, the most probable transition is from the **highest occupied molecular orbital (HOMO)** to the **lowest unoccupied molecular orbital (LUMO)**.


Energy
Four isolated
p orbitals
ψ4*
ψ3*
ψ2
ψ1
Antibonding
(3 nodes)
Antibonding
(2 nodes)
Bonding
(1 node)
Bonding
(0 nodes)



- Since the electron is promoted from a bonding π molecular orbital to an antibonding π^* molecular orbital, we call this a $\pi \rightarrow \pi^*$ excitation (*pi to pi star*).
- The energy gap between the HOMO and the LUMO of 1,3-butadiene is such that UV light of **217** nm wavelength is required to accomplish the $\pi \rightarrow \pi^*$ electronic transition.

- The lowest-energy occupied molecular orbitals are the σ orbitals, which correspond to σ bonds.
- The π orbitals lie at somewhat higher energy levels.
- Orbitals that hold unshared pairs, the **nonbonding** (***n***) orbitals, lie at higher energies.
- The unoccupied, or **antibonding** orbitals (π* and σ*), are the orbitals of the highest energy.

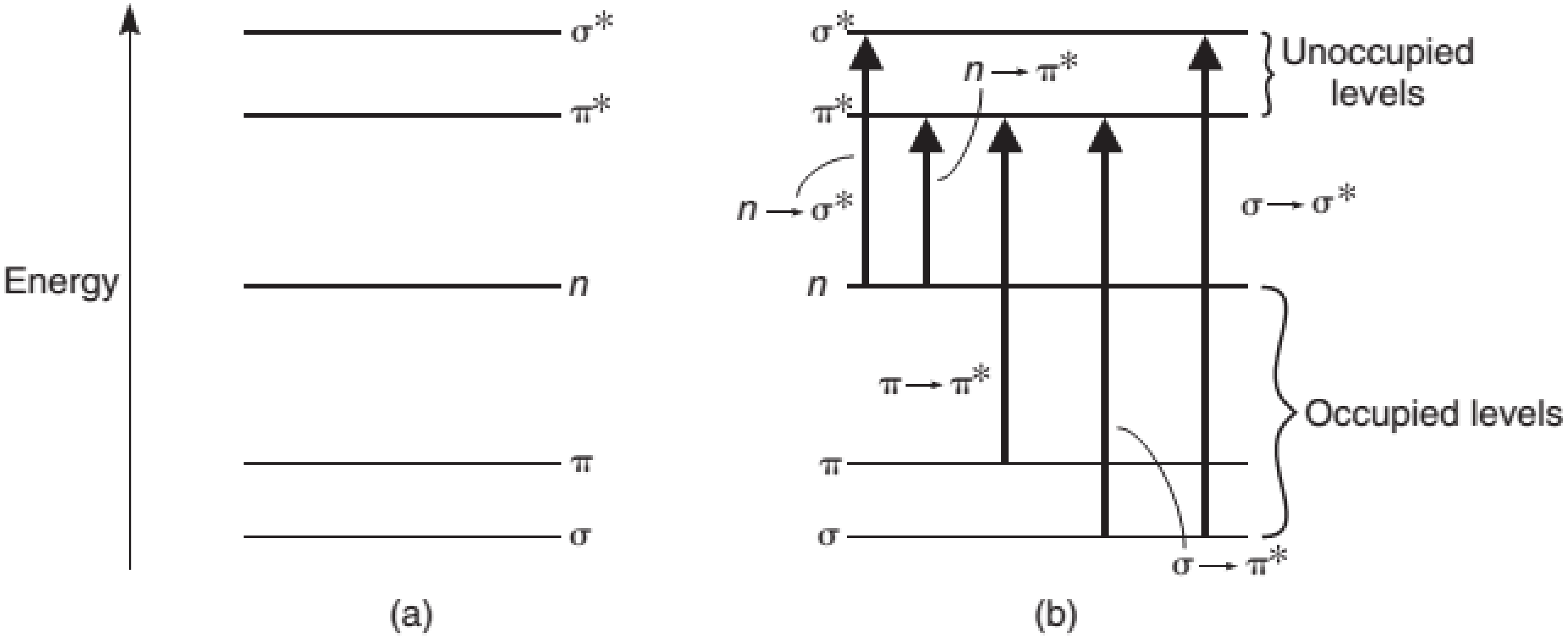
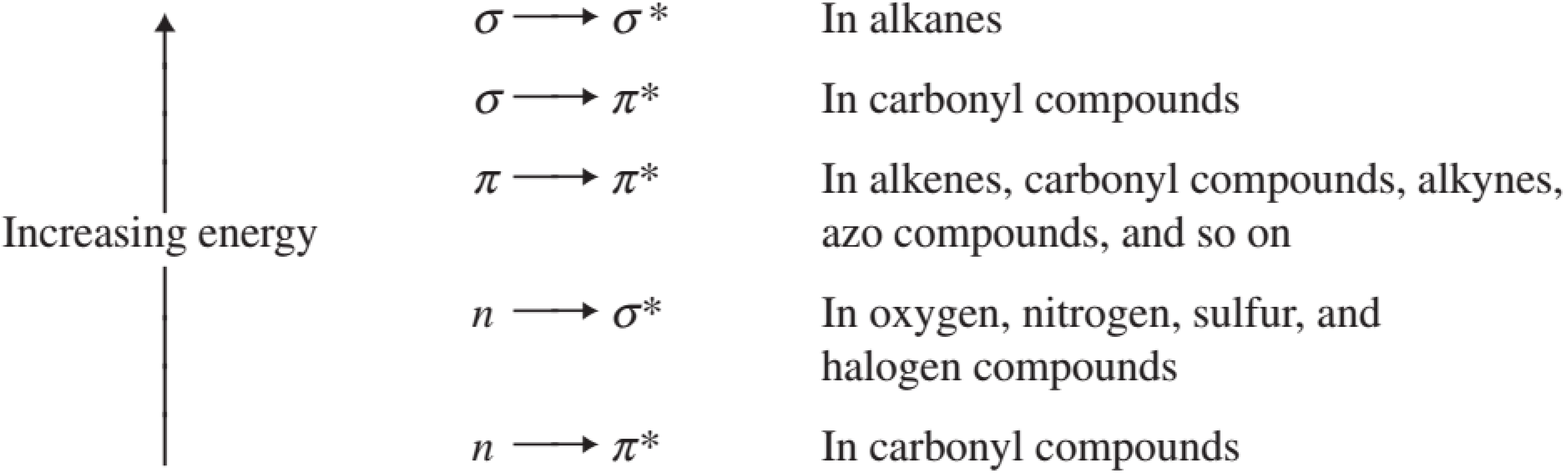


FIGURE 10.2 Electronic energy levels and transitions.

- In all compounds other than alkanes, the electrons may undergo several possible transitions of different energies. Some of the most important transitions are:



Increasing energy

$\sigma \longrightarrow \sigma^*$	In alkanes
$\sigma \longrightarrow \pi^*$	In carbonyl compounds
$\pi \longrightarrow \pi^*$	In alkenes, carbonyl compounds, alkynes, azo compounds, and so on
$n \longrightarrow \sigma^*$	In oxygen, nitrogen, sulfur, and halogen compounds
$n \longrightarrow \pi^*$	In carbonyl compounds

Selection rules

- *Not all of the transitions are observed*. Certain restrictions, called **selection rules**, must be considered.

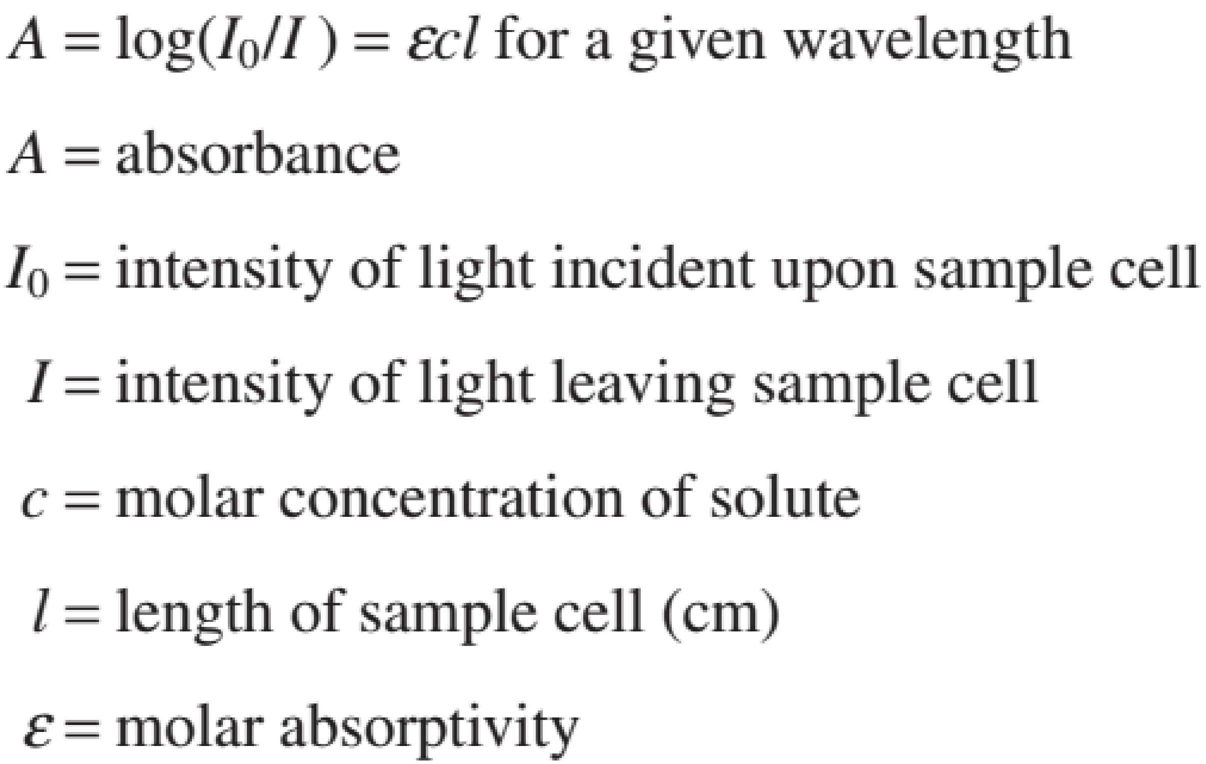
+ Transitions that involve a change in the spin quantum number of an electron during the transition are not allowed to take place; they are called "**forbidden**" transitions.

+ Transitions that are formally forbidden by the selection rules are often not observed.

+ In certain cases, forbidden transitions are observed, but the intensity of the absorption are much lower than for **allowed** transitions.

- The $\boldsymbol{n \rightarrow \pi^*}$ transition is the **most common** type of **forbidden** transition (often observed with ε smaller than 10^3).

The Beer–Lambert Law



$A = \log(I_0/I) = \varepsilon c l$ for a given wavelength

A = absorbance

I_0 = intensity of light incident upon sample cell

I = intensity of light leaving sample cell

c = molar concentration of solute

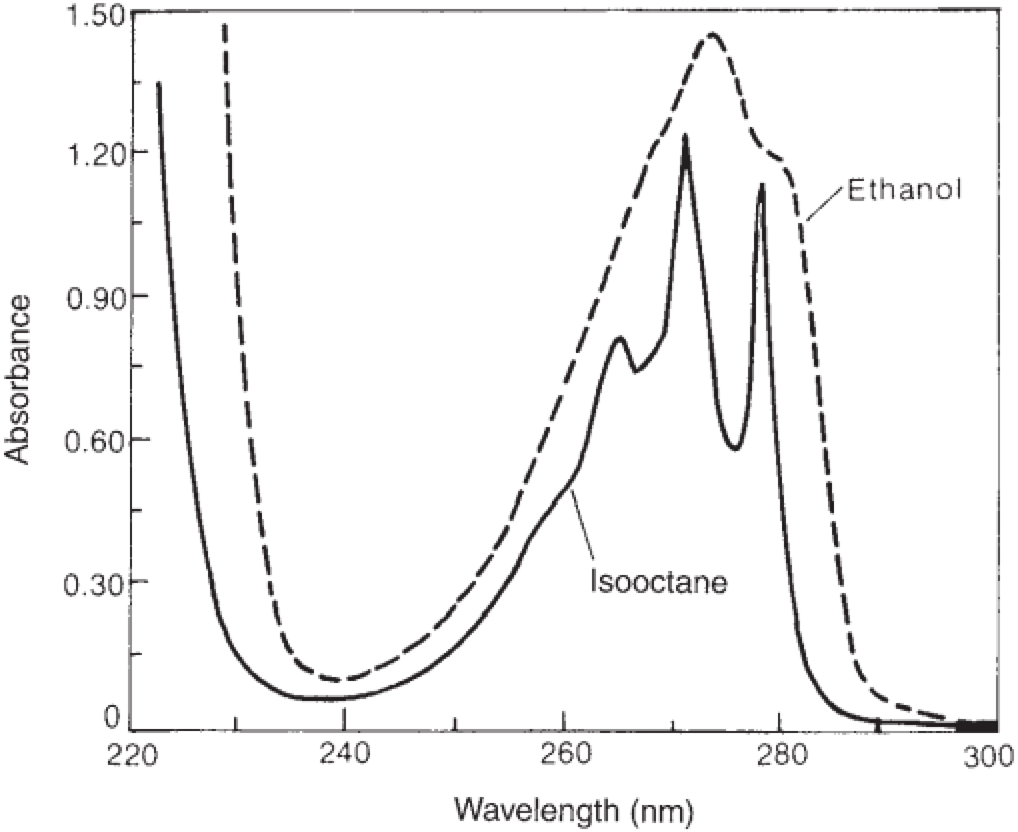
l = length of sample cell (cm)

ε = molar absorptivity

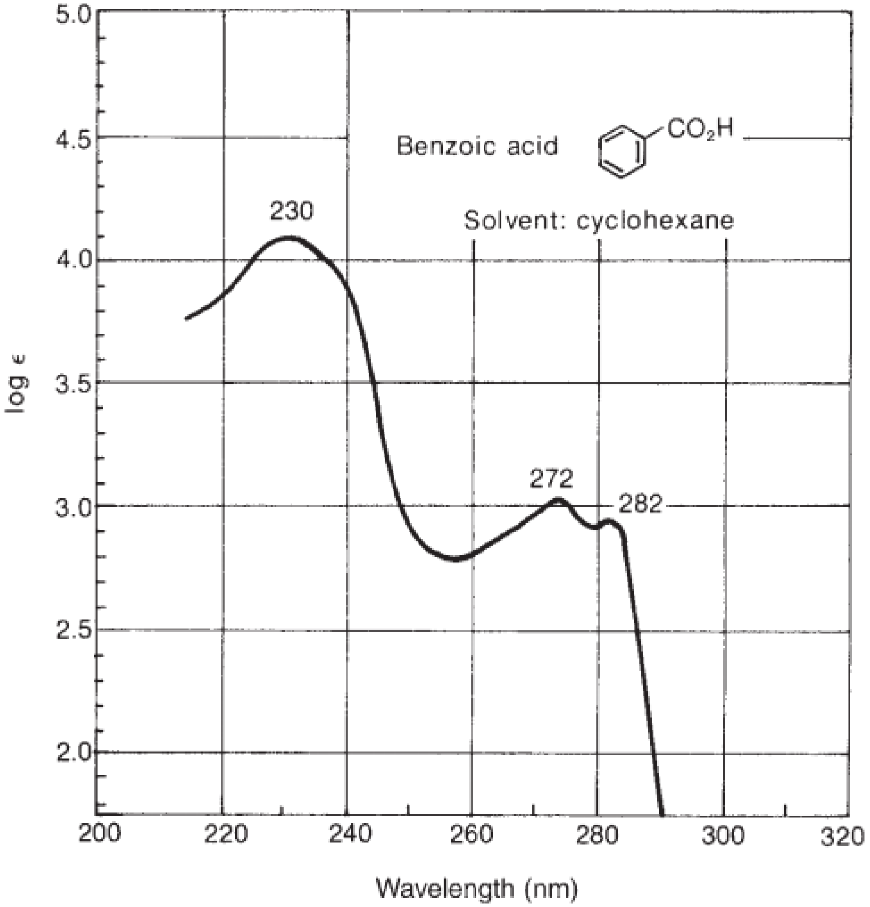
- The **molar absorptivity** (formerly known as the **molar extinction coefficient**) is a typical property of the molecule.
- Molar absorptivities above **10^4** are termed **high-intensity absorptions,** while values below **10^3** are **low-intensity absorptions.**
- Forbidden transitions have absorptivities in the range from 0 to 1000.

PRESENTATION OF SPECTRA

- The UV spectrum of a molecule usually consists of a broad **band** of absorption centered near the wavelength of the major transition.
- The ultraviolet–visible spectrum is generally recorded as a plot of **absorbance** versus **wavelength**.
- It is customary to then re-plot the data with either ε or **logε** plotted on the **y-axis** and wavelength plotted on the x-axis.

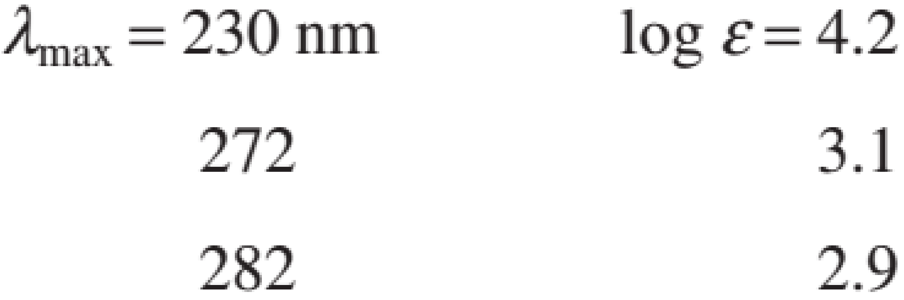


Ultraviolet spectra of phenol in ethanol and in isooctane



PRESENTATION OF SPECTRA

- However, most spectra are described by indications of the wavelength maxima and absorptivities of the principal absorption peaks. For benzoic acid, a typical description might be:



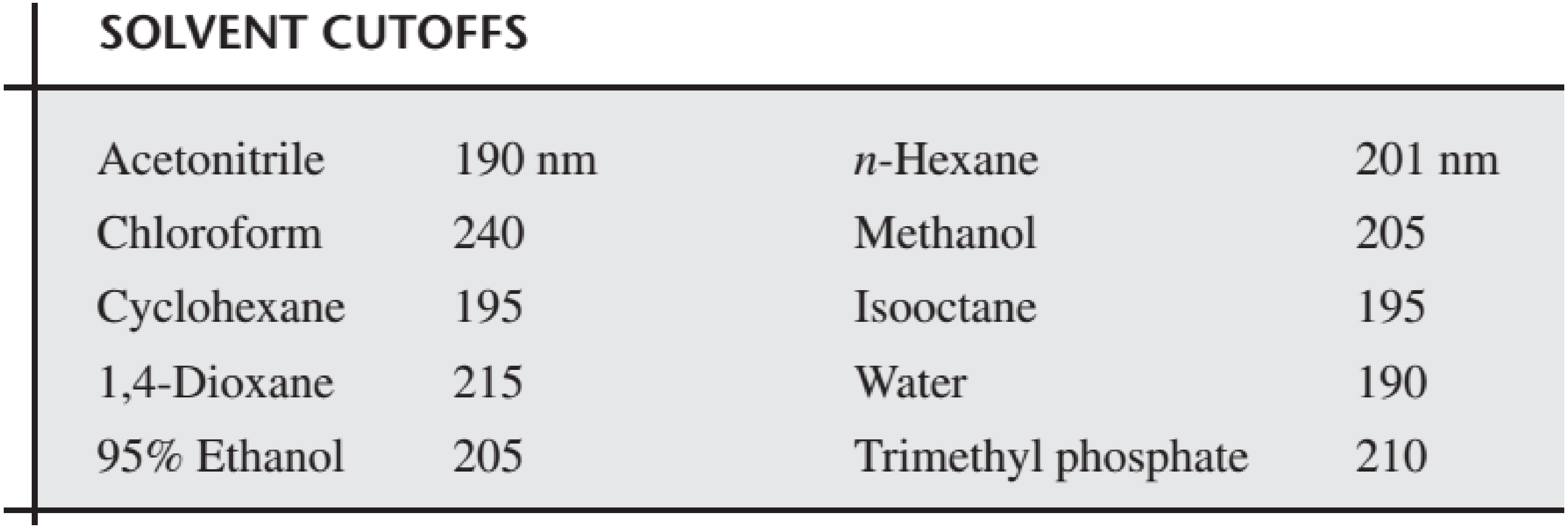
$\lambda_{max} = 230$ nm	$\log \varepsilon = 4.2$
272	3.1
282	2.9

- The figure in the previous slide is the actual spectrum that corresponds to these data.

SOLVENTS

- The first criterion for a good solvent is that it should not absorb ultraviolet radiation in the same region as the substance whose spectrum is being determined.

+ Usually, solvents that do not contain conjugated systems are most suitable for this purpose.



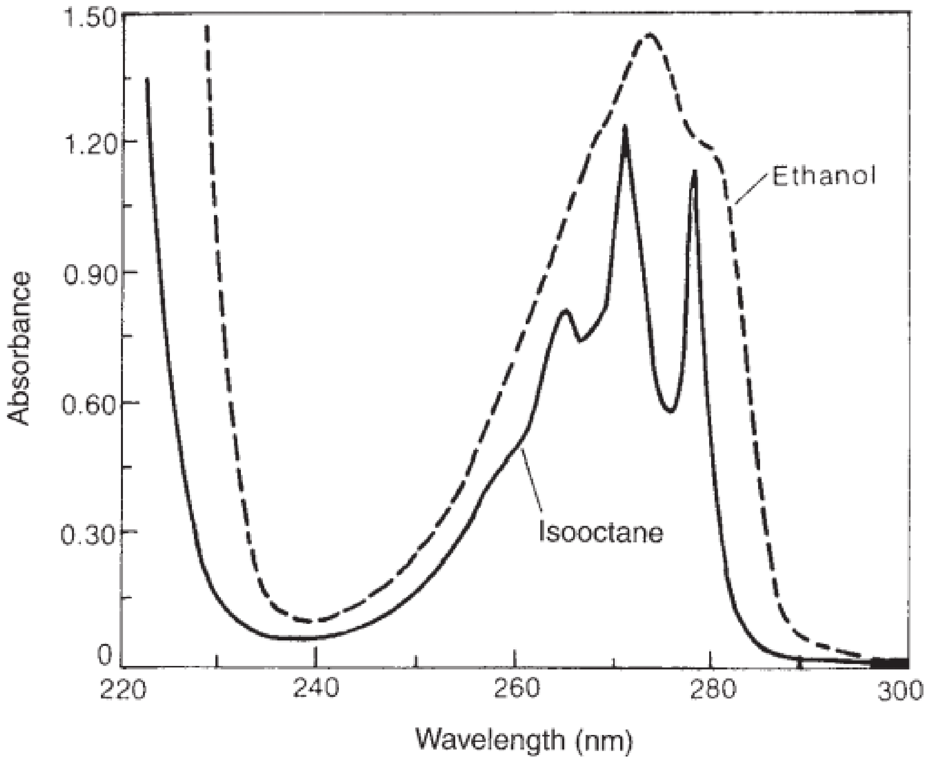
SOLVENT CUTOFFS

Acetonitrile	190 nm	*n*-Hexane	201 nm
Chloroform	240	Methanol	205
Cyclohexane	195	Isooctane	195
1,4-Dioxane	215	Water	190
95% Ethanol	205	Trimethyl phosphate	210

SOLVENTS

+ A nonpolar solvent does not hydrogen bond with the solute, and the spectrum of the solute closely approximates the spectrum that would be produced in the gaseous state, in which fine structure is often observed.

+ In a polar solvent, the hydrogen bonding forms a solute–solvent complex, and the fine structure may disappear.



Ultraviolet spectra of phenol in ethanol and in isooctane.

CHROMOPHORE

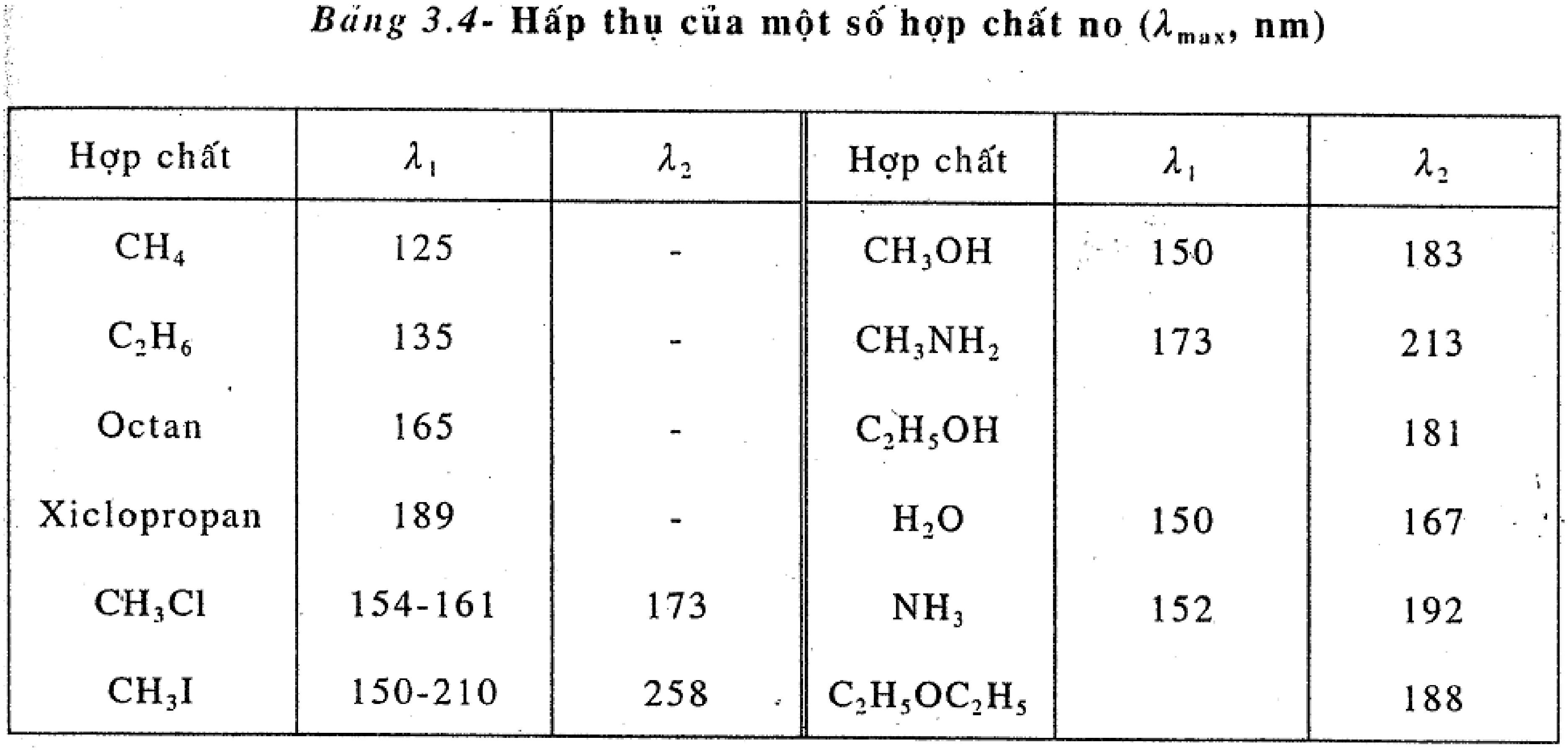
- The characteristic energy of a transition and the wavelength of radiation absorbed are properties of a group of atoms rather than of electrons themselves.

- The group of atoms (**functional groups**) producing such an absorption is called a **chromophore**.

CHROMOPHORE: Alkanes

+ Alkanes contain only single bonds, hence, the only electronic transitions possible are of the σ → σ* type.

+ These transitions are of such a high energy that they absorb ultraviolet energy at very short wavelengths.



Bảng 3.4- **Hấp thụ của một số hợp chất no (λ_{max}, nm)**

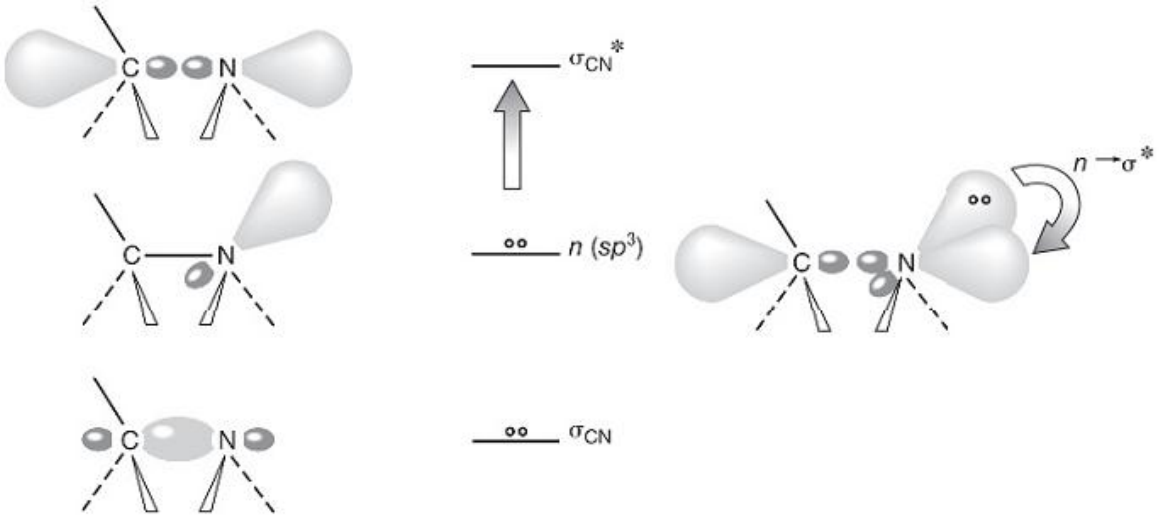
Hợp chất	λ_1	λ_2	Hợp chất	λ_1	λ_2
CH_4	125	-	CH_3OH	150	183
C_2H_6	135	-	CH_3NH_2	173	213
Octan	165	-	C_2H_5OH		181
Xiclopropan	189	-	H_2O	150	167
CH_3Cl	154-161	173	NH_3	152	192
CH_3I	150-210	258	$C_2H_5OC_2H_5$		188

CHROMOPHORE: Alcohols, ethers, amines, and sulfur compounds

- In saturated molecules that contain atoms bearing nonbonding pairs of electrons, transitions of the $n \rightarrow \sigma^*$ type become important.

- Alcohols and amines absorb in the range from 175 to 200 nm, while organic thiols and sulfides absorb between 200 and 220 nm.

- Most of the absorptions are below the cut-off points for the common solvents, so they are not observed in solution spectra.



$n \rightarrow \sigma^*$ transition

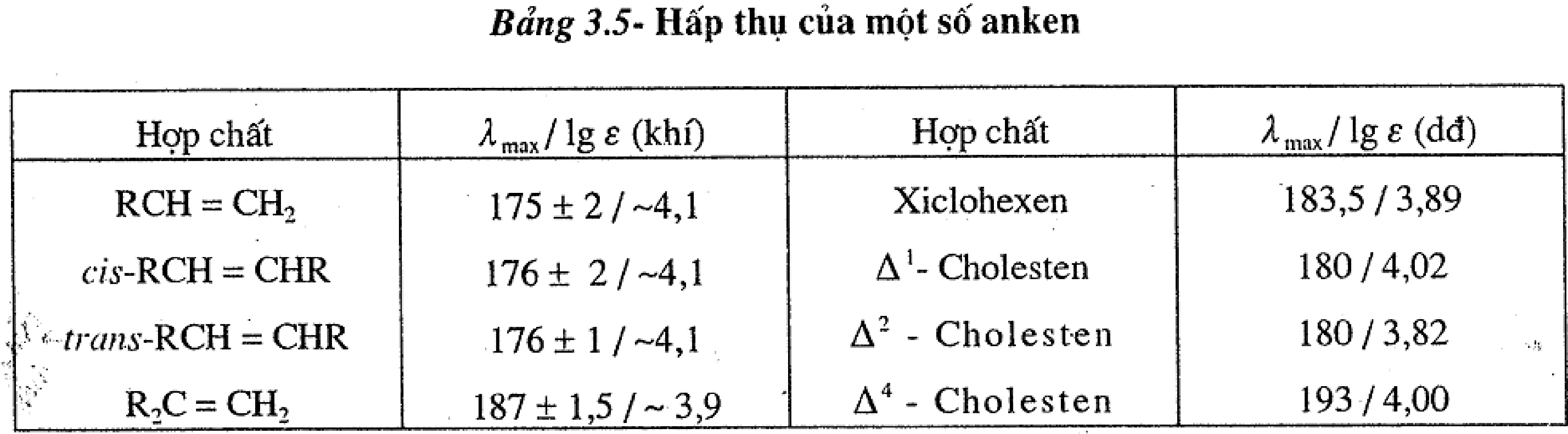
CHROMOPHORE: Alkenes and Alkynes

+ With **unsaturated molecules, π → π* transitions become possible**.

+ These transitions are of rather high energy.

+ Their positions are sensitive to the presence of substitution.

+ Alkenes absorb around 175 nm, and alkynes absorb around 170 nm.



***Bảng 3.5*- Hấp thụ của một số anken**

Hợp chất	λ_{max} / lg ε (khí)	Hợp chất	λ_{max} / lg ε (dđ)
$RCH = CH_2$	175 ± 2 / ~4,1	Xiclohexen	183,5 / 3,89
cis-$RCH = CHR$	176 ± 2 / ~4,1	Δ^1- Cholesten	180 / 4,02
trans-$RCH = CHR$	176 ± 1 / ~4,1	Δ^2 - Cholesten	180 / 3,82
$R_2C = CH_2$	187 ± 1,5 / ~ 3,9	Δ^4 - Cholesten	193 / 4,00

CHROMOPHORE: Carbonyl Compounds

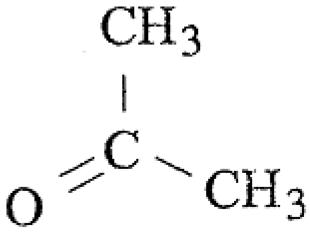
+ Unsaturated molecules that contain atoms such as oxygen or nitrogen may also undergo ***n*** **→ π*** transitions.

+ These transitions are also rather sensitive to substitution on the chromophore.

+ The typical carbonyl compound undergoes an ***n*** **→ π*** transition around **280 to 290 nm** (**ε = 15**).

+ Most ***n*** **→ π*** transitions are forbidden and hence are of low intensity.

+ Carbonyl compounds also have a **π → π*** transition at about **188 nm** (**ε = 900**).

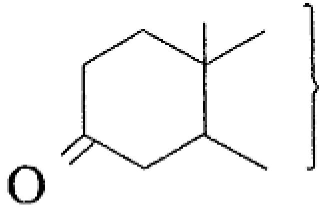


I

277 / 17

188 / 1800

(trong *iso*octan)



II

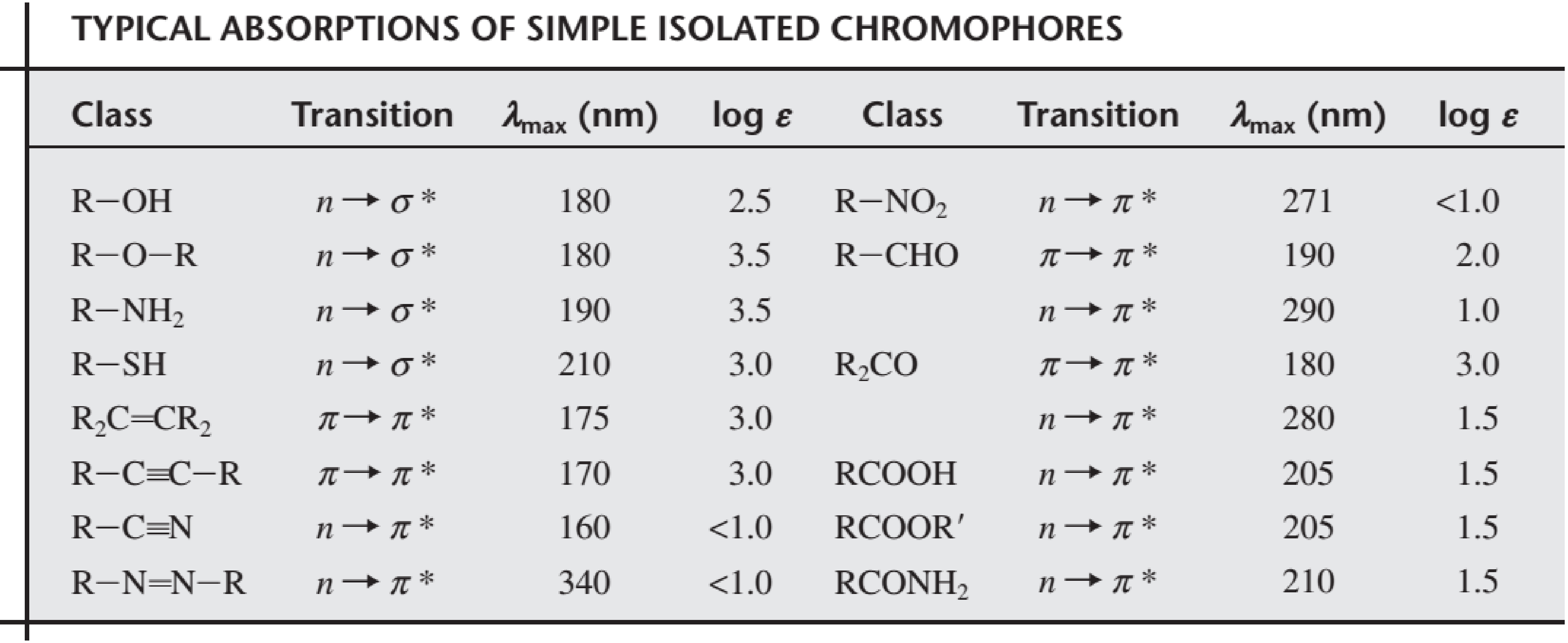
280 / 15

178 / 4460

(trong xyclohexan)

CHROMOPHORE: alcohols, ethers, amines, and sulfur compounds

- This table lists typical absorptions of simple isolated chromophores.
- These *simple* chromophores nearly all absorb at approximately the same wavelength (160 to 210 nm).



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

CHROMOPHORE and auxochromes

- The attachment of substituent groups on a basic **chromophore** structure changes the position and intensity of absorption bands of the chromophore.

- Substituents that increase the intensity of the absorption, and possibly the wavelength, are called **auxochromes** (*for example: methyl, hydroxyl, alkoxy, halogen, and amino groups*).

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

1. **Bathochromic shift** (**red** shift) - a shift to lower energy or **longer** wavelength.
2. **Hypsochromic shift** (**blue** shift) - a shift to higher energy or **shorter** wavelength.
3. **Hyperchromic effect**—an increase in intensity.
4. **Hypochromic effect**—a decrease in intensity.

THE EFFECT OF CONJUGATION

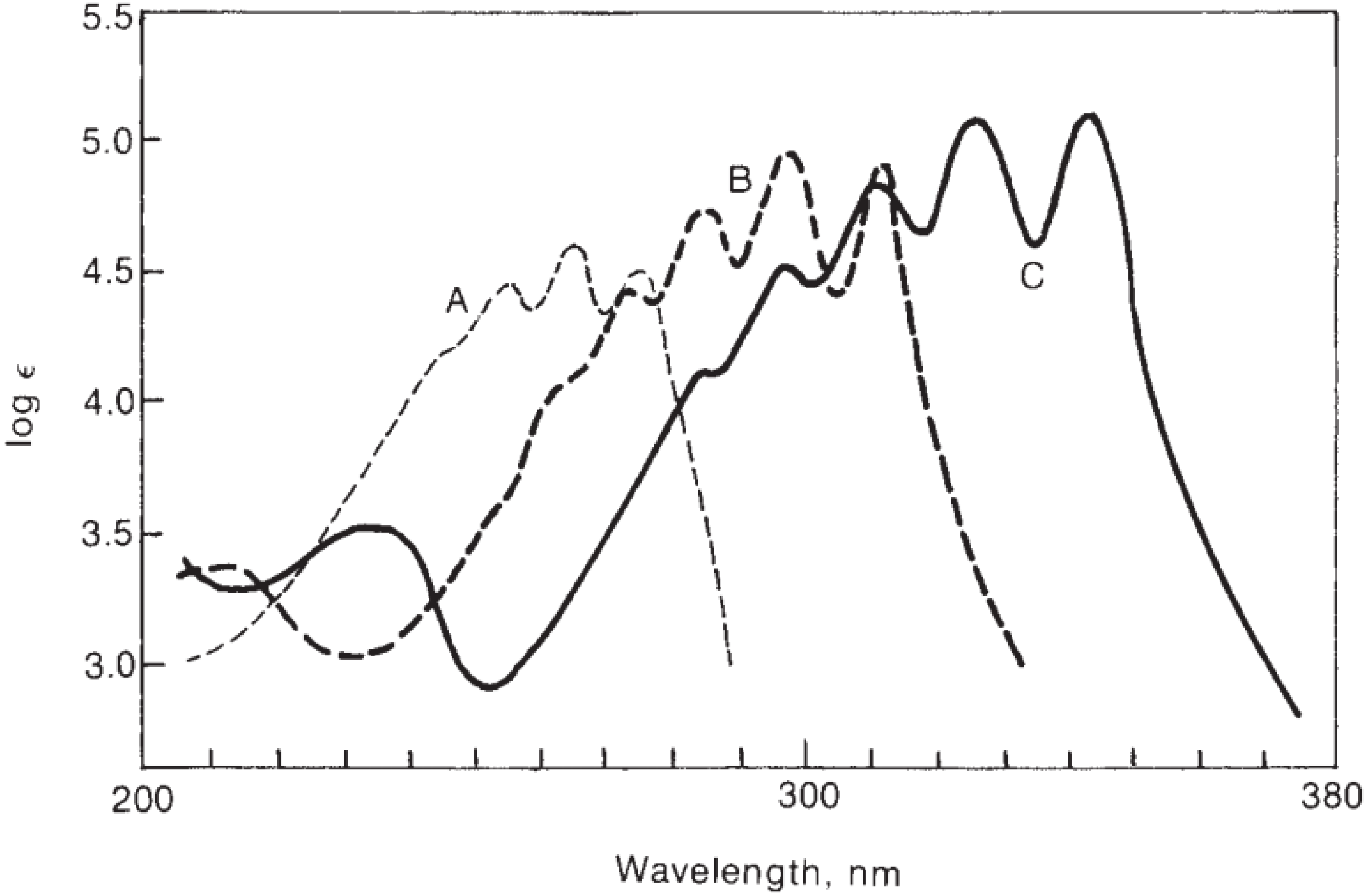
- One of the best ways to bring about a bathochromic shift is to increase the extent of conjugation in a double-bonded system.

- In the presence of conjugated double bonds, the electronic energy levels of a chromophore move closer together.

+ As a result, the energy required to produce a transition from an **occupied** electronic energy level to an **unoccupied** level decreases, and the wavelength of the light absorbed becomes longer.

THE EFFECT OF CONJUGATION

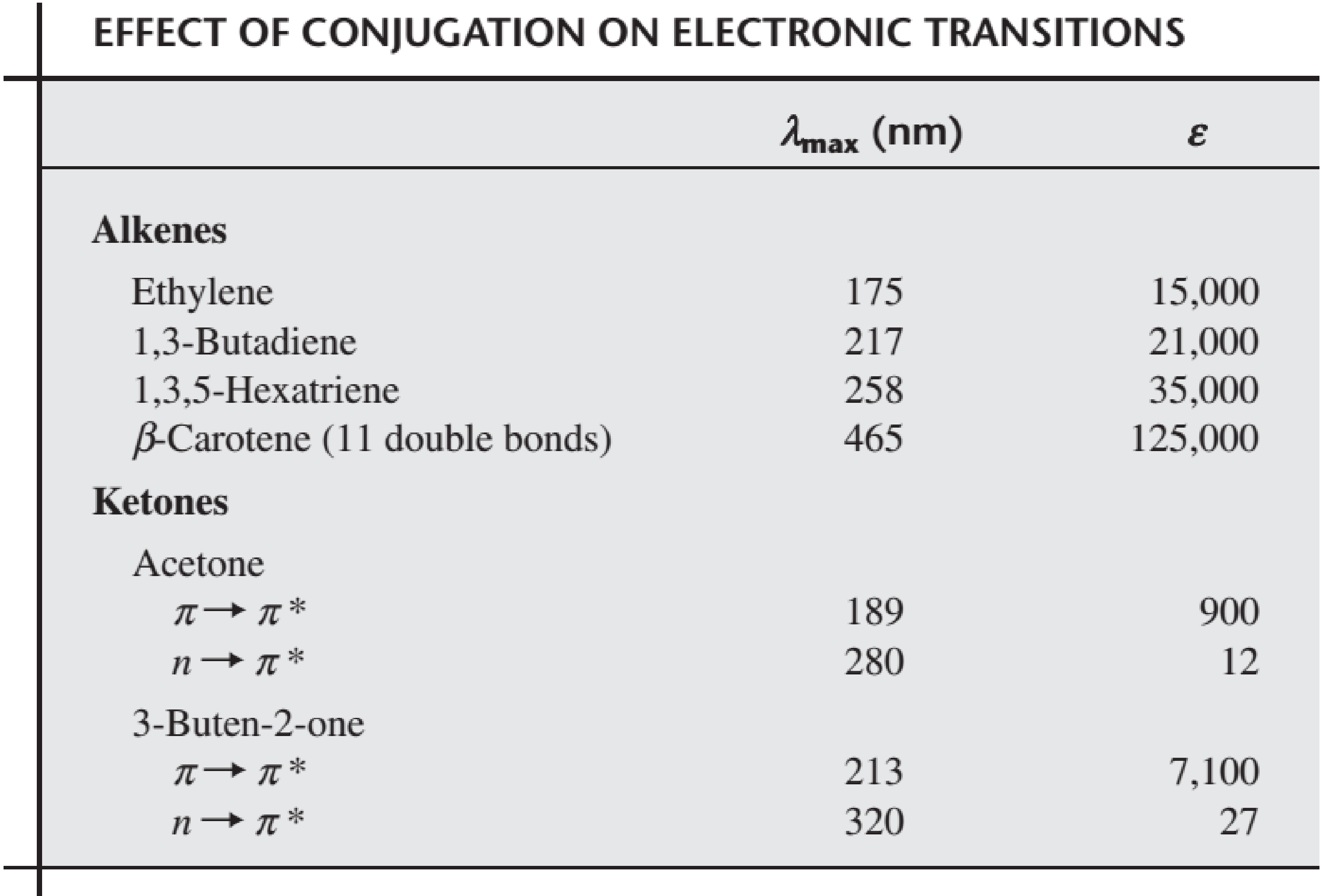
➢ This figure illustrates the bathochromic shift in a series of conjugated polyenes as the length of the conjugated chain is increased.



CH_3-$(CH{=}CH)_n$-CH_3 ultraviolet spectra of dimethylpolyenes. (**A**) $n = 3$; (**B**) $n = 4$; (**C**) $n = 5$.

THE EFFECT OF CONJUGATION

- Conjugation of two chromophores not only results in a bathochromic shift but also increases the intensity of the absorption.
- The exact position and intensity of the absorption band can be correlated with the extent of conjugation.



EFFECT OF CONJUGATION ON ELECTRONIC TRANSITIONS

	λ_{max} (nm)	ε
Alkenes		
Ethylene	175	15,000
1,3-Butadiene	217	21,000
1,3,5-Hexatriene	258	35,000
β-Carotene (11 double bonds)	465	125,000
Ketones		
Acetone		
$\pi \rightarrow \pi^*$	189	900
$n \rightarrow \pi^*$	280	12
3-Buten-2-one		
$\pi \rightarrow \pi^*$	213	7,100
$n \rightarrow \pi^*$	320	27

THE EFFECT OF CONJUGATION ON ALKENES

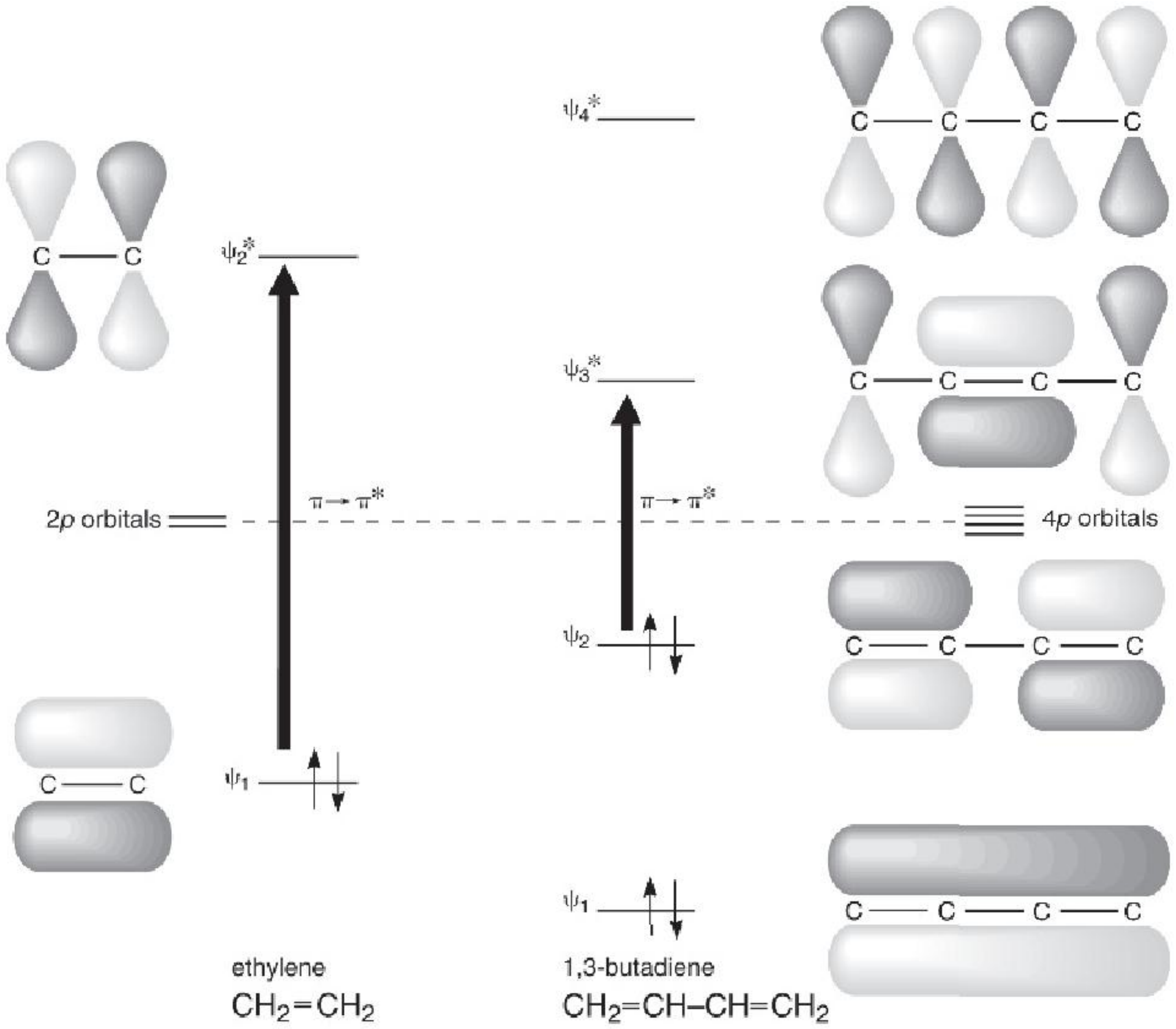


FIGURE 10.12 A comparison of the molecular orbital energy levels and the energy of the $\pi \rightarrow \pi^*$ transitions in ethylene and 1,3-butadiene.

THE EFFECT OF CONJUGATION ON ALKENES

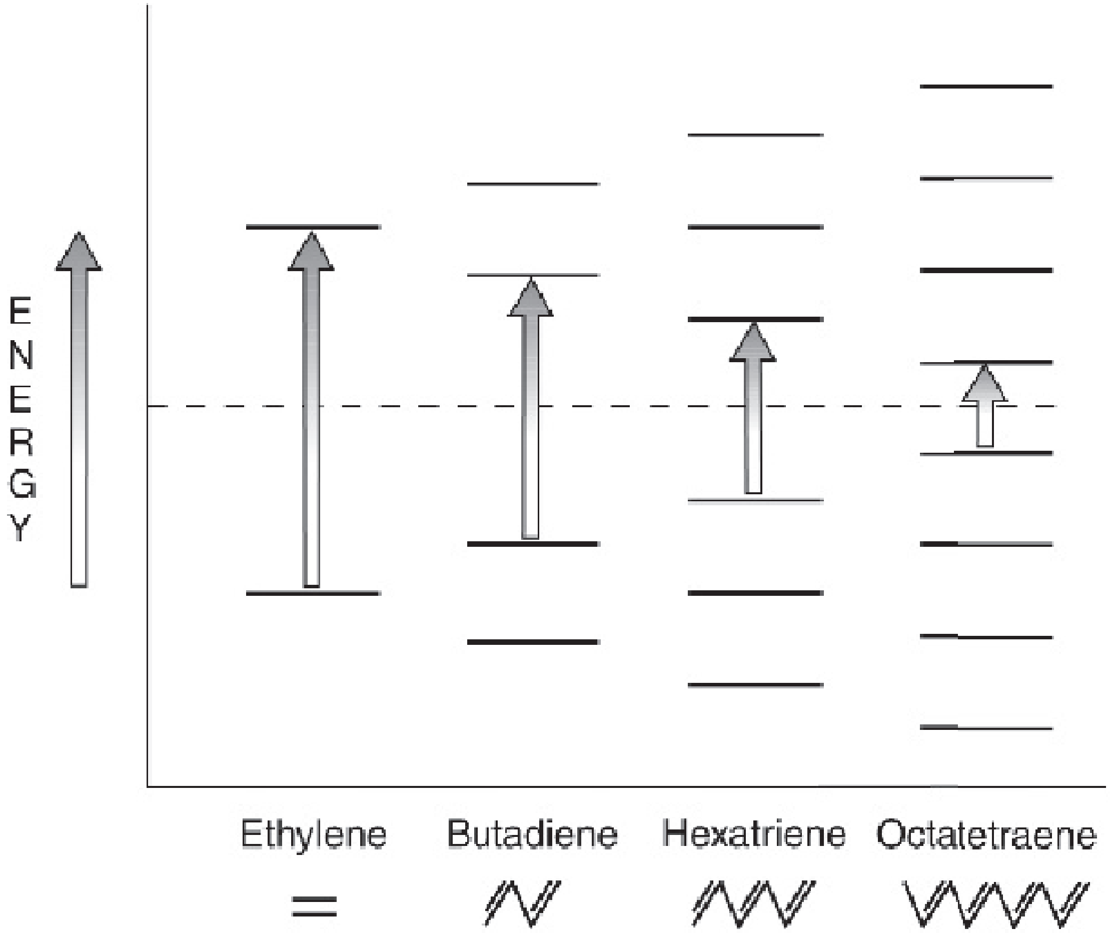
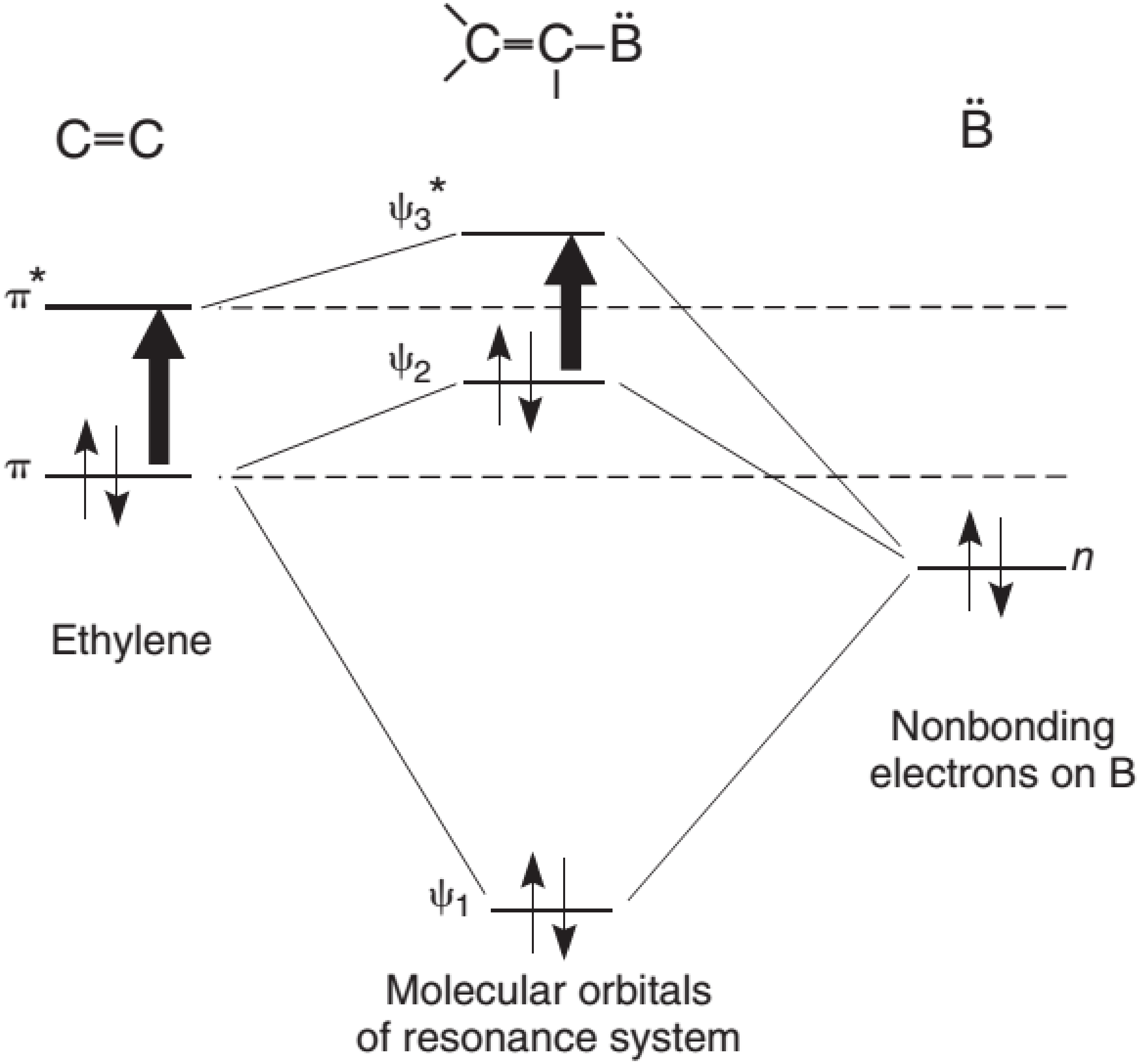


FIGURE 10.13 A comparison of the $\pi \rightarrow \pi^*$ energy gap in a series of polyenes of increasing chain length.

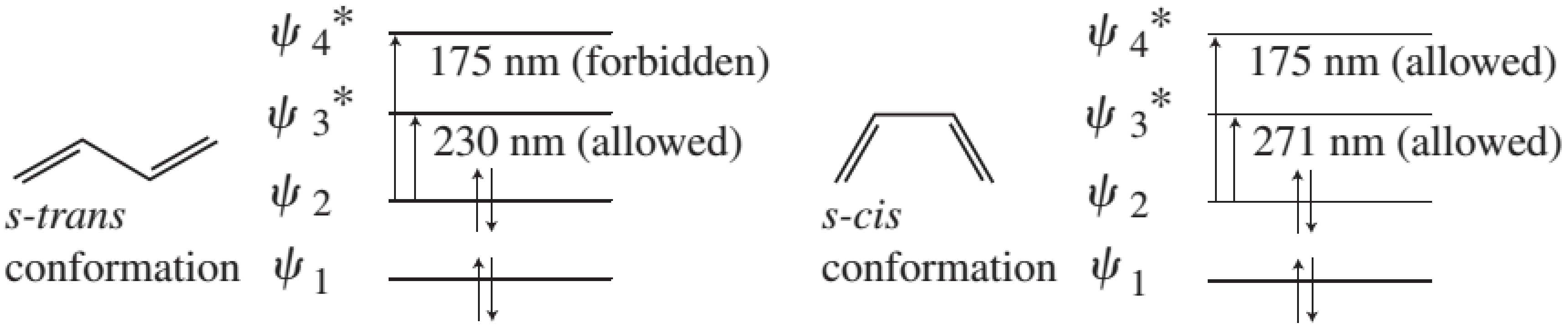
THE EFFECT OF CONJUGATION ON ALKENES



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

THE EFFECT OF CONJUGATION ON ALKENES

- The $\psi_2 \rightarrow \psi_3^*$ transition is easily observable.



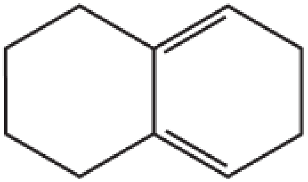
- In general, conjugated dienes exhibit an intense band (ε = 20.000 to 26.000) in the region from 217 to 245 nm, owing to a $\pi \rightarrow \pi^*$ transition.

- The position of this band is quite insensitive to the nature of the solvent.

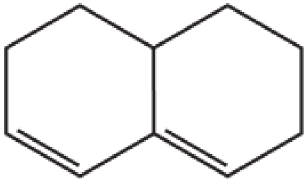
The Woodward and Fieser rules for dienes

- In cyclic dienes, where the central bond is a part of the ring system, the diene chromophore is usually held rigidly in either the *s-trans* (**transoid**) or the *s-cis* (**cisoid**) orientation.

- Typical absorption spectra follow the expected pattern:



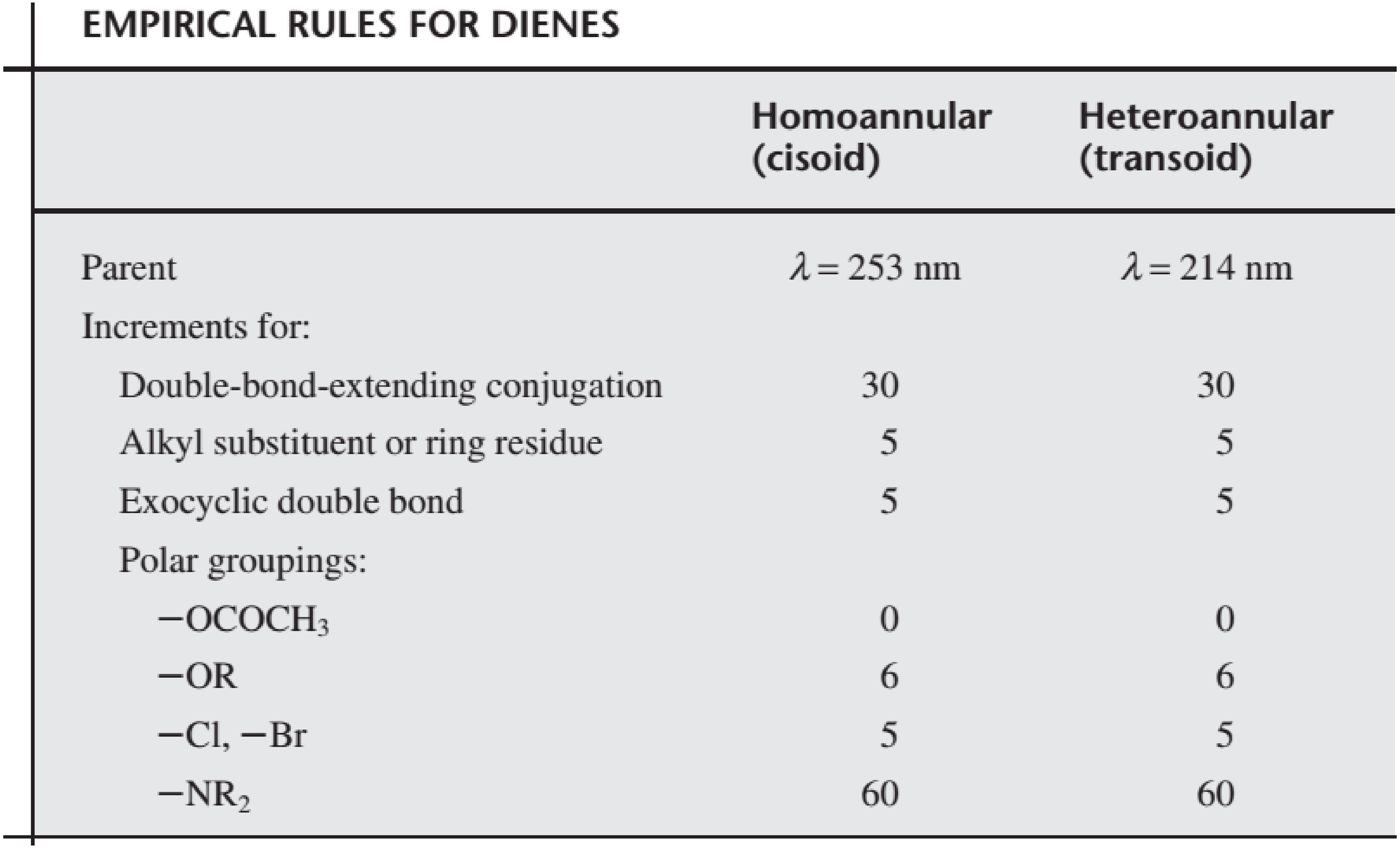
Homoannular diene (cisoid or *s-cis*)
Less intense, ε = 5,000–15,000
λ longer (273 nm)



Heteroannular diene (transoid or *s-trans*)
More intense, ε = 12,000–28,000
λ shorter (234 nm)

The Woodward and Fieser rules for dienes

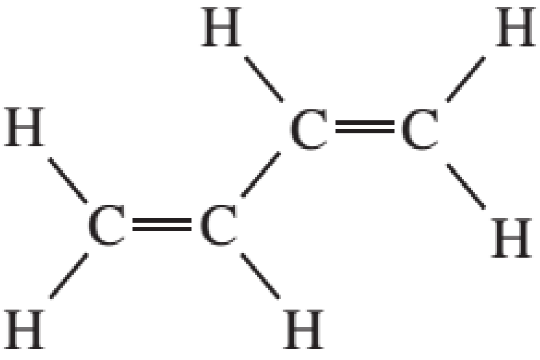
- Woodward and Fieser devised an empirical correlation of structural variations that enables us to predict the wavelength at which a conjugated diene will absorb.



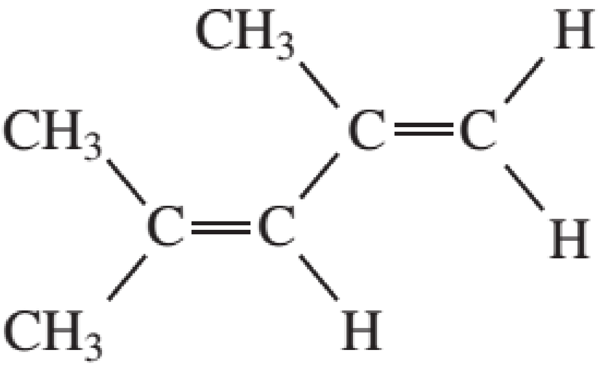
EMPIRICAL RULES FOR DIENES

	Homoannular (cisoid)	Heteroannular (transoid)
Parent	$\lambda = 253$ nm	$\lambda = 214$ nm
Increments for:		
Double-bond-extending conjugation	30	30
Alkyl substituent or ring residue	5	5
Exocyclic double bond	5	5
Polar groupings:		
$-OCOCH_3$	0	0
$-OR$	6	6
$-Cl$, $-Br$	5	5
$-NR_2$	60	60

The Woodward and Fieser rules for dienes



Transoid: 214 nm
Observed: 217 nm



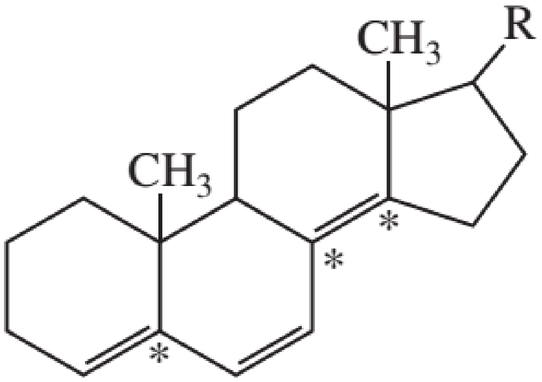
Transoid:	214 nm
Alkyl groups: 3 × 5 =	15
	229 nm
Observed:	228 nm

The Woodward and Fieser rules for dienes

- An *exocyclic double bond* is a double bond that lies outside a given ring.

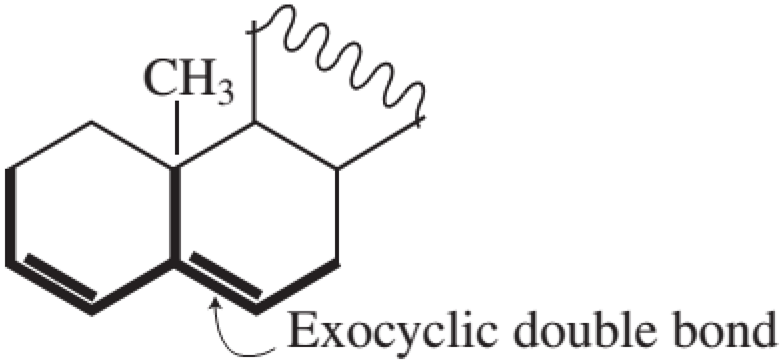
- Notice that the exocyclic bond may lie within one ring even though it is outside another ring.

- Often, an exocyclic double bond will be found at **a junction point** on rings.



Three exocyclic double bonds = 3 × 5 = 15 nm

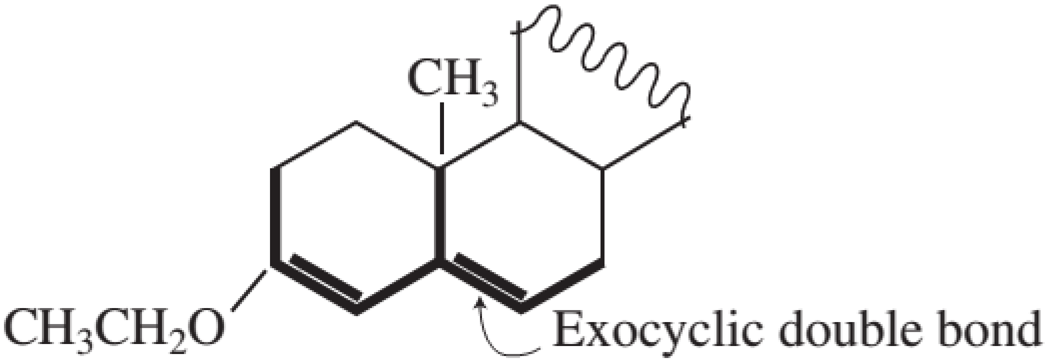
The Woodward and Fieser rules for dienes



Exocyclic double bond

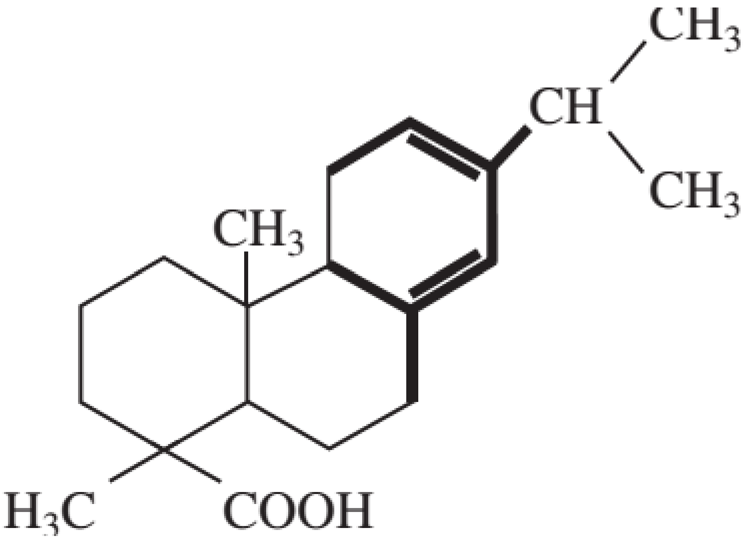
Transoid:	214 nm
Ring residues: 3 × 5 =	15
Exocyclic double bond:	5
	234 nm
Observed:	235 nm

The Woodward and Fieser rules for dienes



Transoid:	214 nm
Ring residues: 3 × 5 =	15
Exocyclic double bond:	5
—OR:	6
	240 nm
Observed:	241 nm

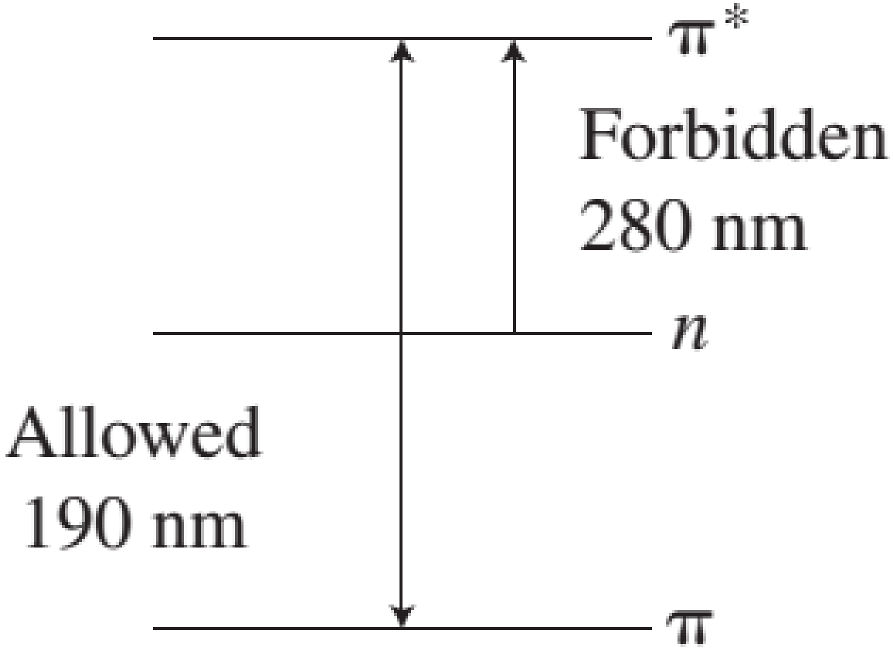
The Woodward and Fieser rules for dienes



Cisoid:	253 nm
Alkyl substituent:	5
Ring residues: 3 × 5 =	15
Exocyclic double bond:	5
	278 nm
Observed:	275 nm

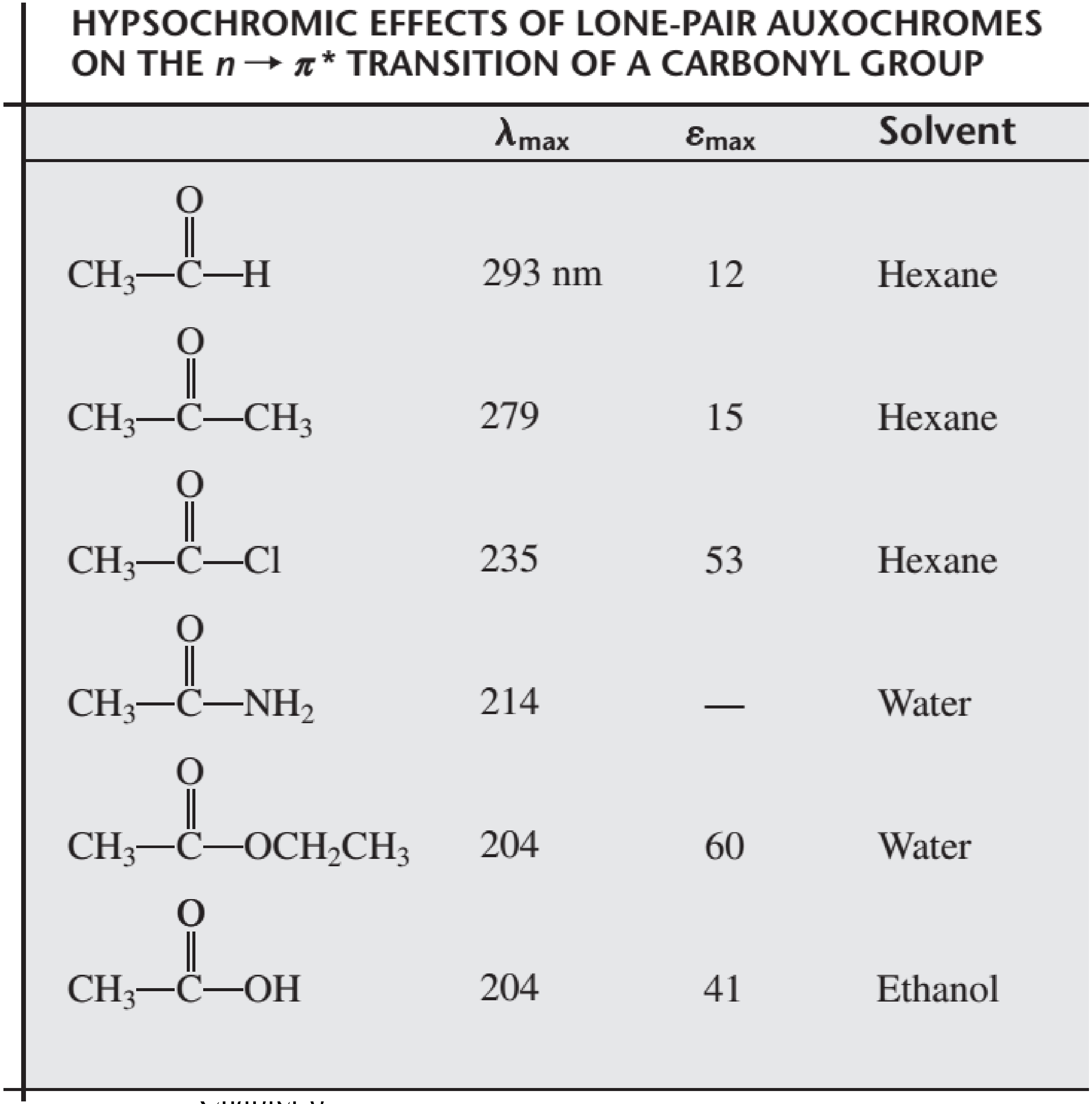
CARBONYL COMPOUNDS

- Carbonyl compounds have two principal UV transitions, the allowed $\pi \rightarrow \pi^*$ transition and the forbidden $n \rightarrow \pi^*$ transition.



- Of these, only the $n \rightarrow$ p * transition, although it is weak (**forbidden**), is commonly observed above the usual cutoff points of solvents.

Substitution on the carbonyl group by an auxochrome with a lone pair of electrons, such as NR_2, OH, OR, NH_2, or X gives a pronounced hypsochromic effect on the $n \rightarrow \pi^*$ transition and a lesser, bathochromic effect on the $\pi \rightarrow \pi^*$ transition.



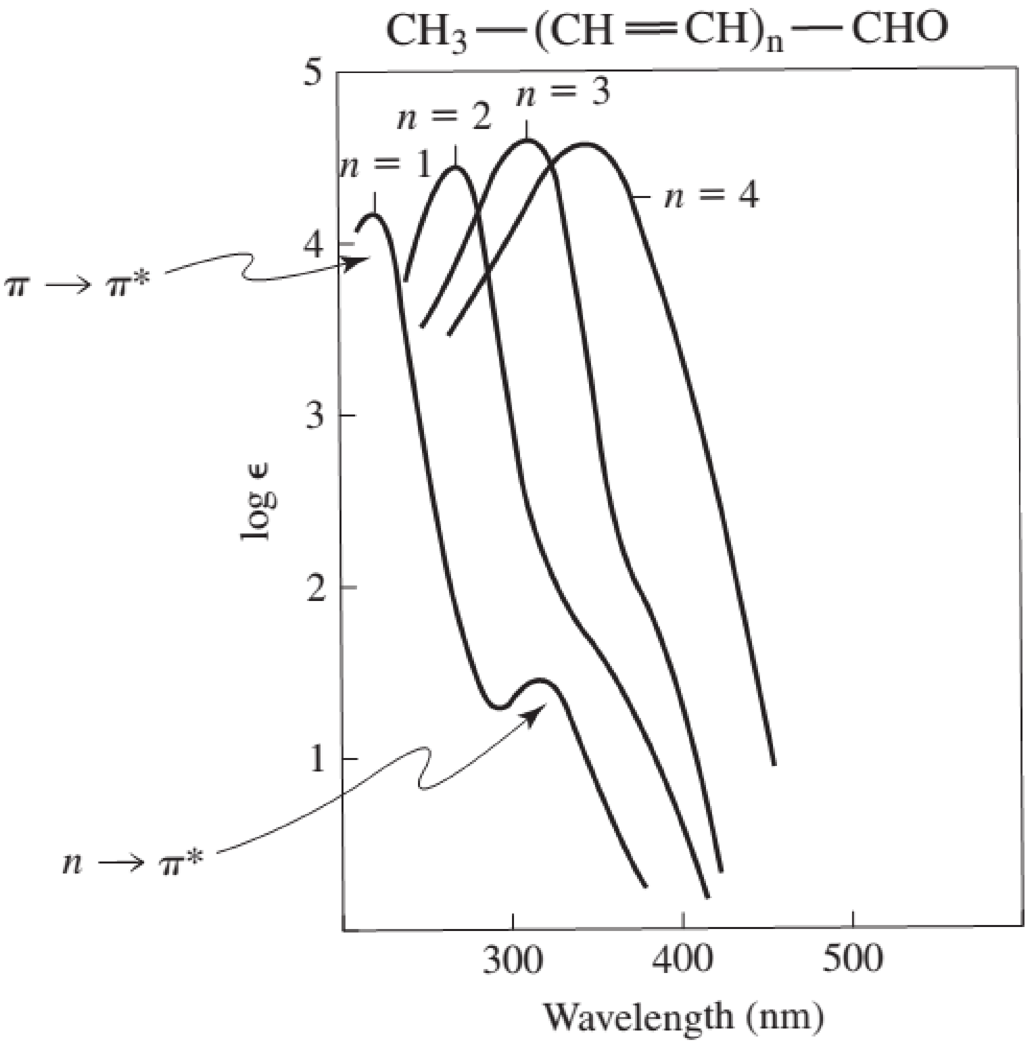
HYPSOCHROMIC EFFECTS OF LONE-PAIR AUXOCHROMES ON THE $n \rightarrow \pi^*$ TRANSITION OF A CARBONYL GROUP

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

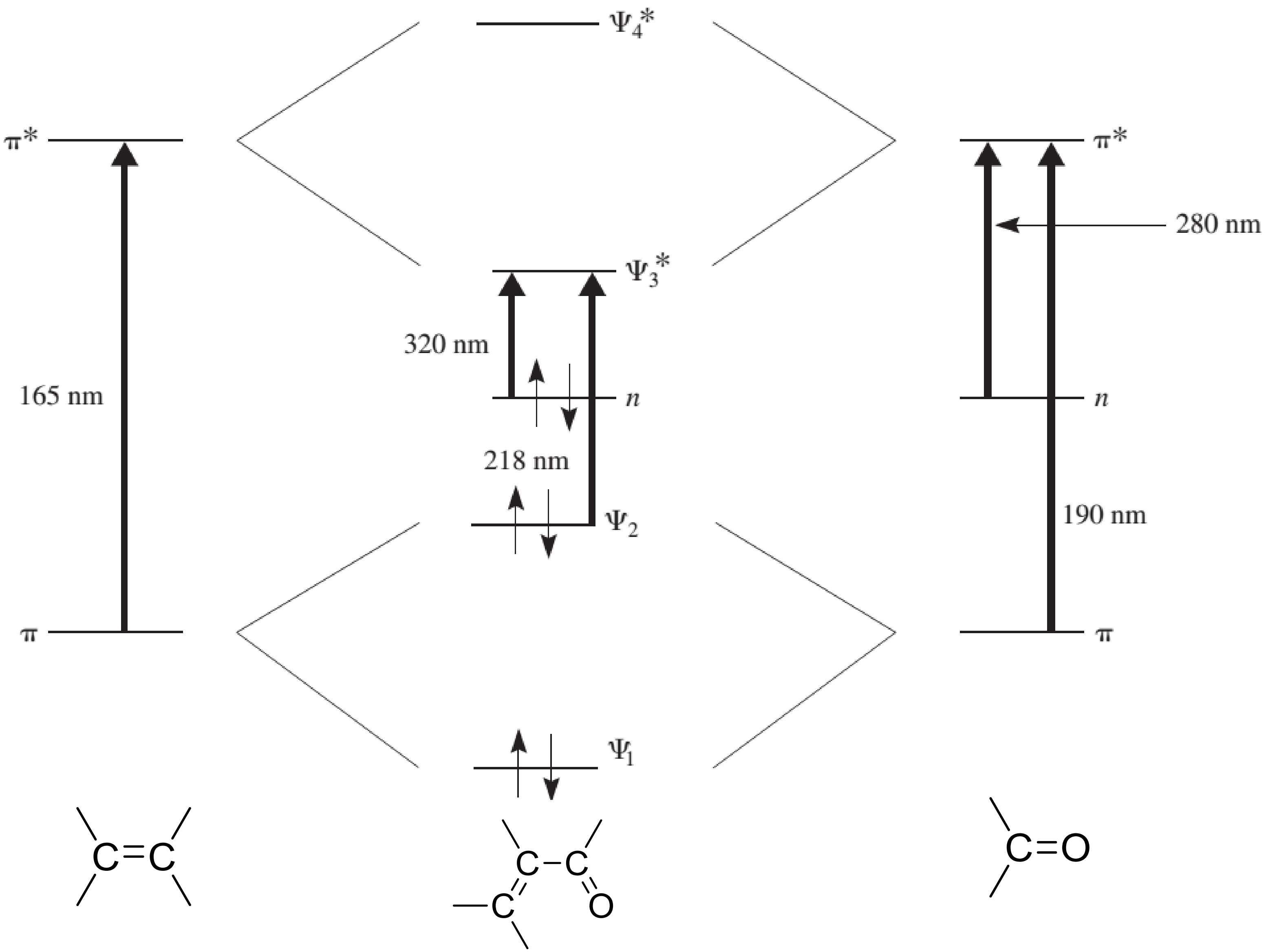
ENONES

- If the carbonyl group is part of a conjugated system, both the *n* → π* and the π → π* bands are shifted to longer wavelengths.

- If the conjugated chain becomes long enough, the *n* → π* band is "buried" under the more intense π → π* band.



ENONES



Enone

Woodward's rules for ENONES

- The conjugation of a double bond with a carbonyl group leads to intense absorption (**ε = 8.000 to 20.000**) corresponding to a **π→π*** transition of the carbonyl group. The absorption is found between **220** and **250** nm in simple enones.

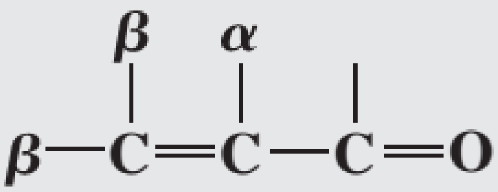
- The *n* → π* transition is much less intense (ε = 50 to 100) and appears at 310 to 330 nm.

- Although the π→π* transition is affected in predictable fashion by structural modifications of the chromophore, the *n*→π* transition does not exhibit such predictable behavior.

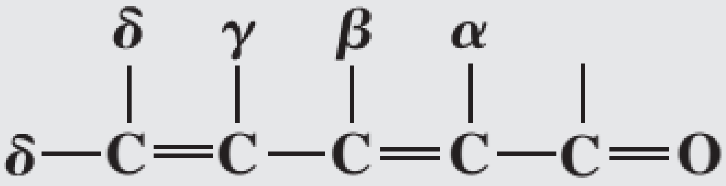
- Woodward examined the ultraviolet spectra of numerous enones and devised a set of empirical rules that enable us to **predict the wavelength** at which the **π→π*** transition occurs in an unknown enone.

ENONES

EMPIRICAL RULES FOR ENONES



$\beta-\overset{\overset{\beta}{|}}{C}=\overset{\overset{\alpha}{|}}{C}-\overset{|}{C}=O$



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

Base values:

Six-membered ring or acyclic parent enone		= 215 nm
Five-membered ring parent enone		= 202 nm
Acyclic dienone		= 245 nm

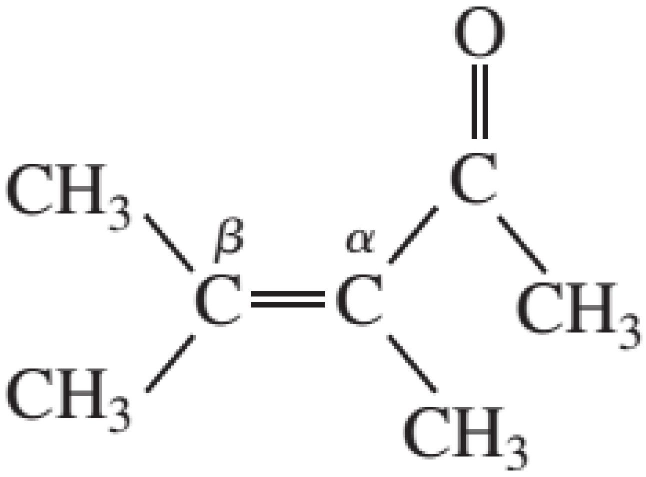
Increments for:

Double-bond-extending conjugation		30
Alkyl group or ring residue	α	10
	β	12
	γ and higher	18

ENONES

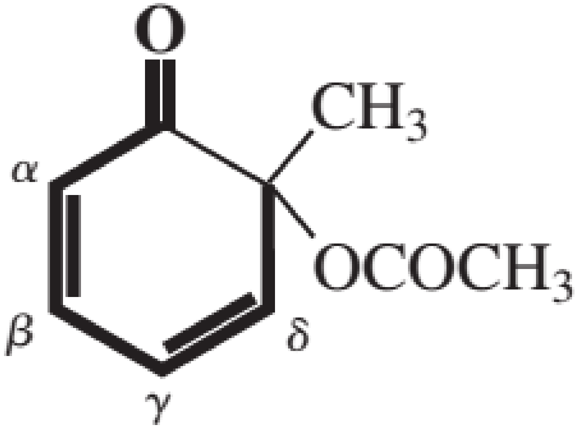
Polar groupings:		
$-OH$	α	35
	β	30
	δ	50
$-OCOCH_3$	α,β,δ	6
$-OCH_3$	α	35
	β	30
	γ	17
	δ	31
$-Cl$	α	15
	β	12
$-Br$	α	25
	β	30
$-NR_2$	β	95
Exocyclic double bond		5
Homocyclic diene component		39
Solvent correction		Variable
		λ_{max}^{EtOH}(calc) = Total

ENONES



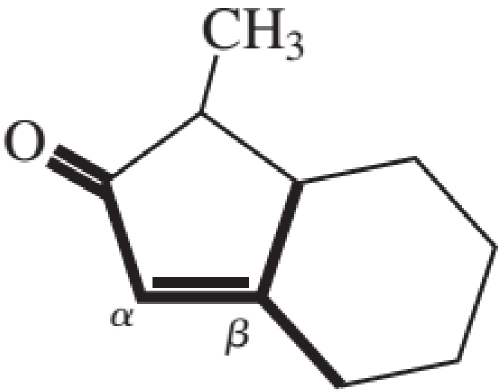
Acyclic enone:	215 nm
α-CH_3:	10
β-CH_3: $2 \times 12 =$	24
	249 nm
Observed:	249 nm

ENONES



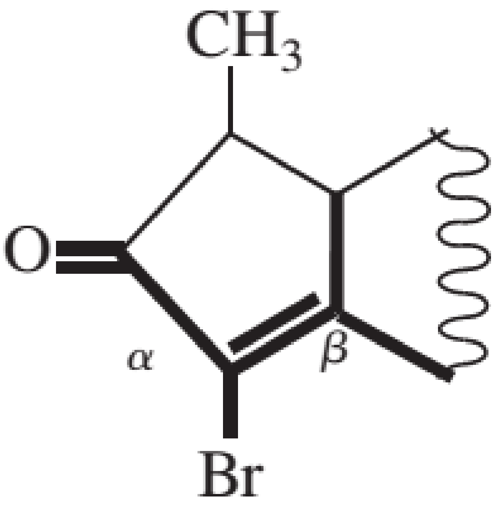
Six-membered enone:	215 nm
Double-bond-extending conjugation:	30
Homocyclic diene:	39
δ-Ring residue:	18
	302 nm
Observed:	300 nm

ENONES



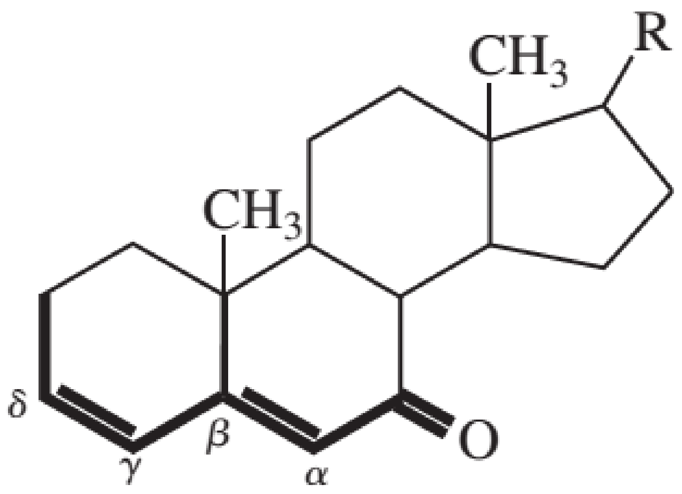
Five-membered enone:	202 nm
β-Ring residue: 2 × 12 =	24
Exocyclic double bond:	5
	231 nm
Observed:	226 nm

ENONES



Five-membered enone:	202 nm
α-Br:	25
β-Ring residue: 2 × 12 =	24
Exocyclic double bond:	5
	256 nm
Observed:	251 nm

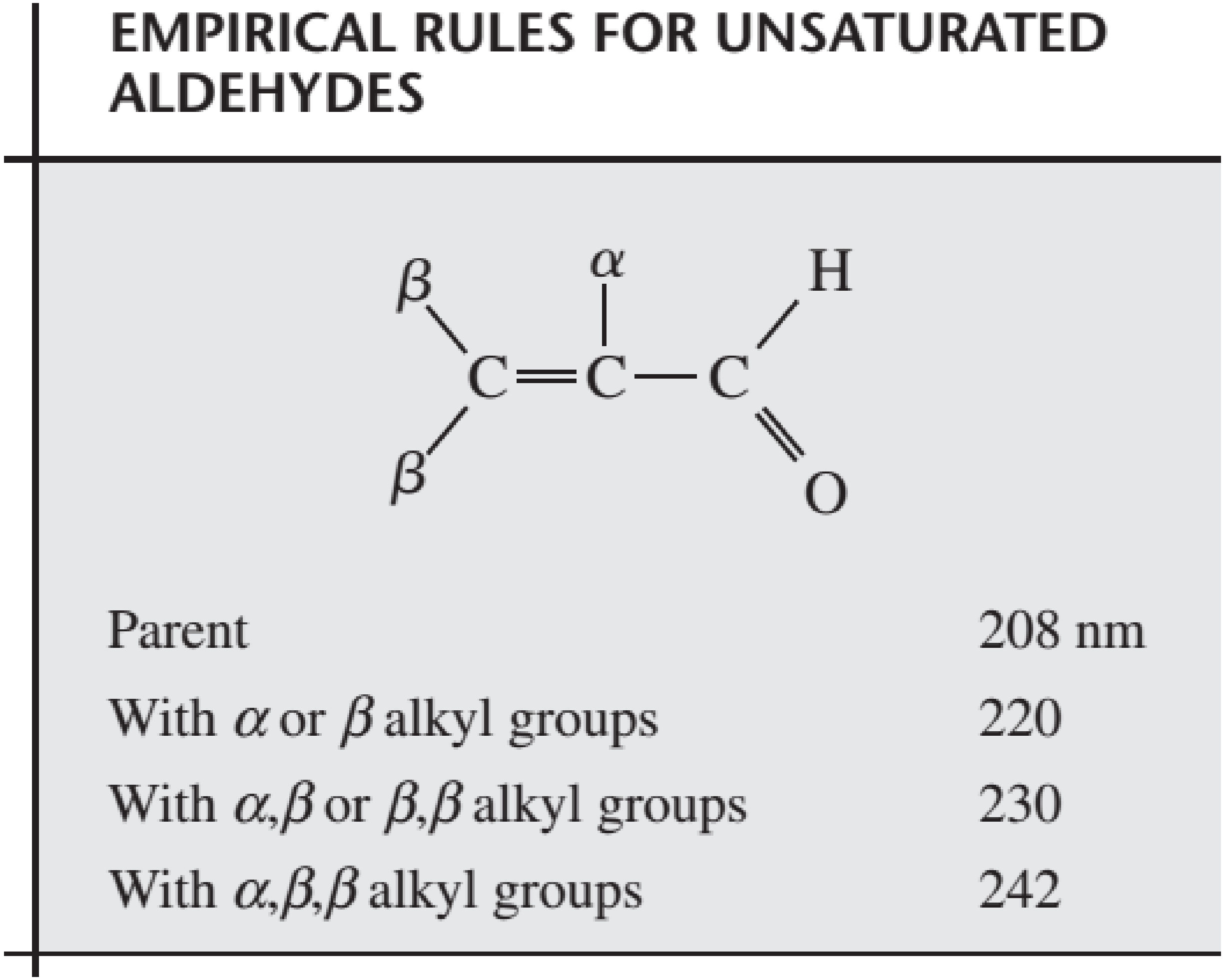
ENONES



Six-membered enone:	215 nm
Double-bond-extending conjugation:	30
β-Ring residue:	12
δ-Ring residue:	18
Exocyclic double bond:	5
	280 nm
Observed:	280 nm

α,β-UNSATURATED ALDEHYDES

- α,β-Unsaturated aldehydes generally follow the same rules as enones except that their absorptions are displaced by about 5 to 8 nm toward shorter wavelength than those of the corresponding ketones.



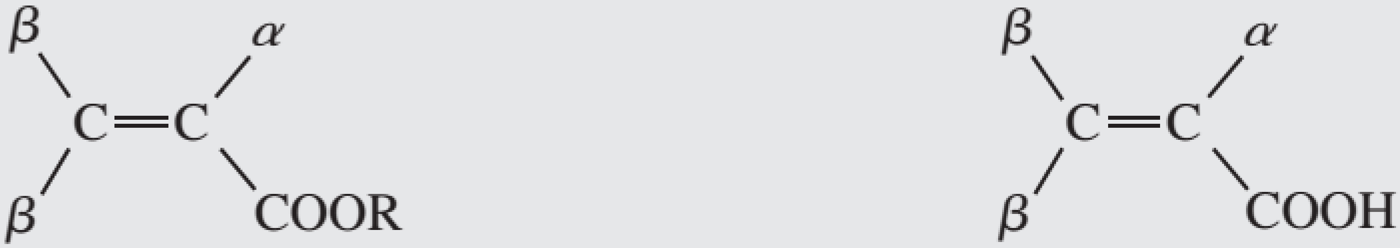
EMPIRICAL RULES FOR UNSATURATED ALDEHYDES

Parent	208 nm
With α or β alkyl groups	220
With α,β or β,β alkyl groups	230
With α,β,β alkyl groups	242

α,β-UNSATURATED ACIDS AND ESTERS

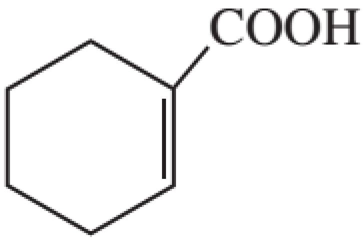
EMPIRICAL RULES FOR UNSATURATED ACIDS AND ESTERS

Base values for:

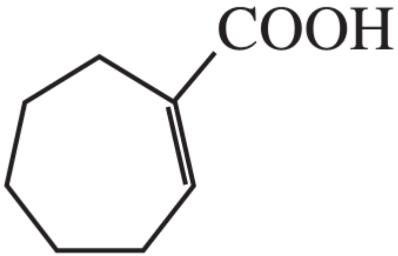


With *α* or *β* alkyl group	208 nm
With *α*,*β* or *β*,*β* alkyl groups	217
With *α*,*β*,*β* alkyl groups	225
For an exocyclic *α*,*β* double bond	Add 5 nm
For an endocyclic *α*,*β* double bond in a five- or seven-membered ring	Add 5 nm

α,β-UNSATURATED ACIDS AND ESTERS



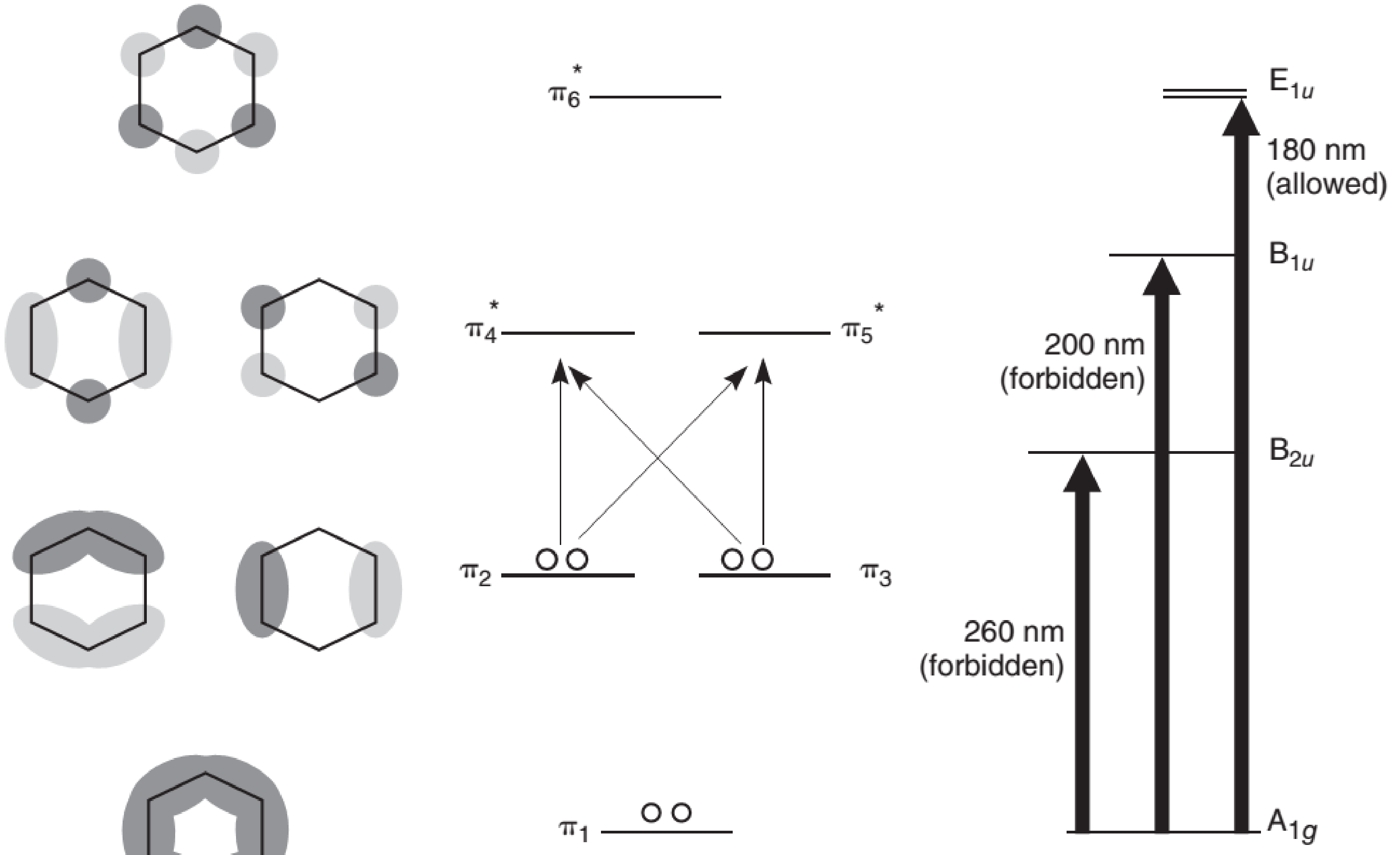
α,*β*-dialkyl	217 nm calc.
Double bond is in a six-membered ring, adds nothing	217 nm obs.



α,*β*-dialkyl	217 nm
Double bond is in a seven-membered ring	+ 5
	222 nm calc.
	222 nm obs.

AROMATIC COMPOUNDS

- The ultraviolet spectrum of the **benzene chromophore** contains **three** absorption bands.
- The electronic transitions are basically of the $\pi \rightarrow \pi^*$ type.



(a) Molecular orbitals

(b) Energy states

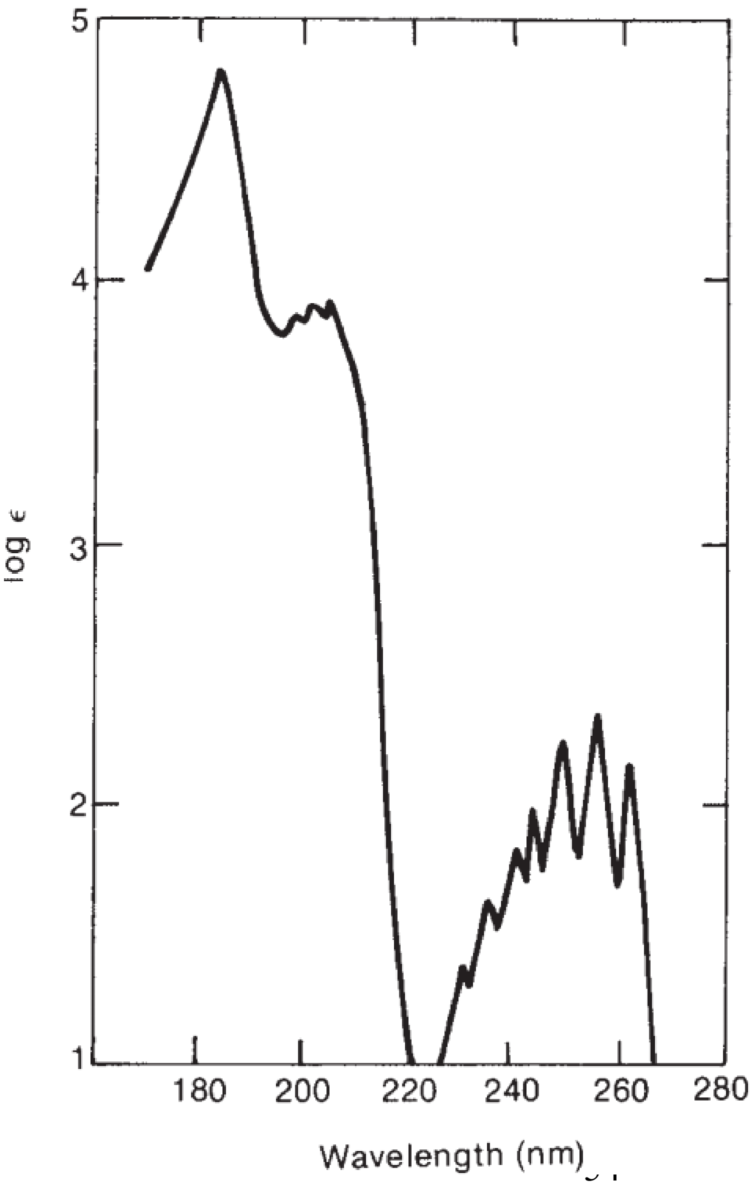
AROMATIC COMPOUNDS

- The three transitions are the **primary bands** at 184 and 202 nm and the **secondary** (*fine-structure*) **band** at 255 nm.

\+ The 184-nm band has a molar absorptivity of 47.000 (*an allowed transition*). Nevertheless, this transition is normally not observed because absorptions at this wavelength are beyond the range of most commercial instruments.

\+ The 202-nm band is much less intense ($\varepsilon = 7400$; *a forbidden transition*).

\+ The 255-nm band is the least intense ($\varepsilon = 230$, *a symmetry-forbidden electronic transition*).



AROMATIC COMPOUNDS

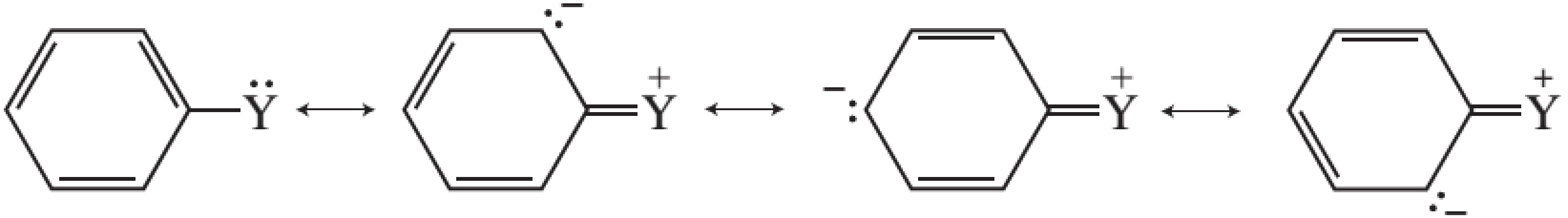
- Substitution on the benzene ring can cause bathochromic and hyperchromic shifts.

- *Unfortunately, these shifts are difficult to predict. Consequently, it is impossible to formulate empirical rules to predict the spectra of aromatic substances as was done for dienes and enones*.

- We may gain a qualitative understanding of the effects of substitution by classifying substituents into groups.

AROMATIC COMPOUNDS: Substituents with unshared electrons

- Substituents with non-bonding electrons can **increase the length of the π system** through resonance.



- Examples of groups with *n* electrons are the amino, hydroxyl, and methoxy groups, as well as the halogens.
- Interactions between the *n* and π electrons usually cause shifts in the primary and secondary benzene absorption bands **to longer wavelength**.
- The more available these *n* electrons are for interaction with the π system, the greater the shifts will be.
- In addition, the presence of *n* electrons in these compounds gives the possibility of *n*→π* transitions.

AROMATIC COMPOUNDS: Substituents with unshared electrons

➢ In compounds that are acids or bases, pH changes can have very significant effects on the positions of the primary and secondary bands.

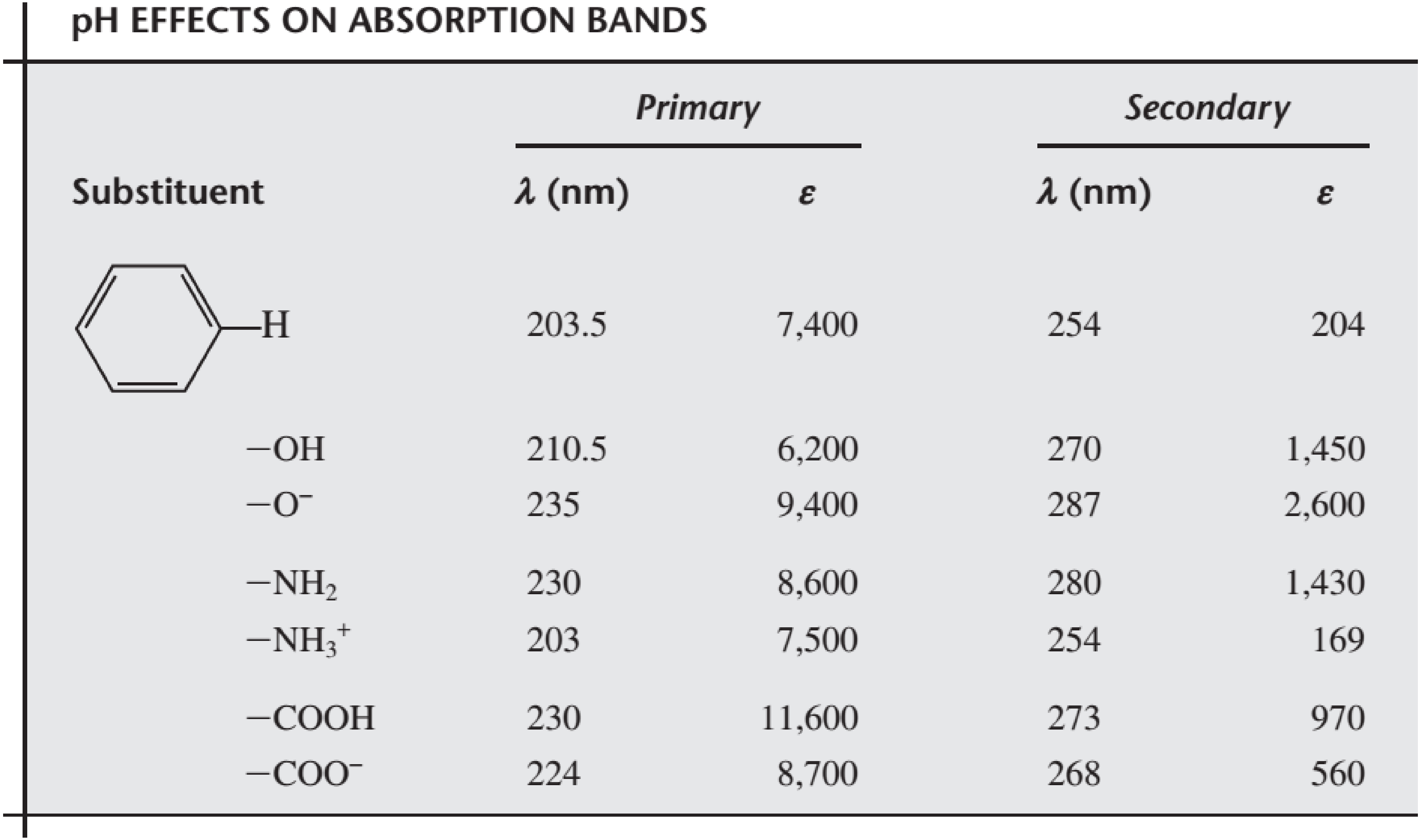
\+ In phenol, the primary band shifts from 203.5 to 210.5 nm (a 7-nm shift); The secondary band shifts from 254 to 270 nm (a 16-nm shift).

\+ In phenoxide ion, the primary band shifts from 203.5 to 235 nm (a 31.5-nm shift), and the secondary band shifts from 254 to 287 nm (a 33-nm shift).

\+ The intensity of the secondary band also increases.

➢ In phenoxide ion, there are more *n* electrons, and they are more available for interaction with the aromatic π system than in phenol.

AROMATIC COMPOUNDS: Substituents with unshared electrons



pH EFFECTS ON ABSORPTION BANDS

Substituent	Primary λ (nm)	Primary ε	Secondary λ (nm)	Secondary 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

AROMATIC COMPOUNDS: Substituents with unshared electrons

➢ Aniline and anilinium ion illustrate a reverse case.

\+ From benzene to aniline, the primary band shifts from 203.5 to 230 nm (a 26.5-nm shift), and the secondary band shifts from 254 to 280 nm (a 26-nm shift). Aniline exhibits shifts similar to those of phenol.

\+ These large shifts are not observed in the case of anilinium ion.

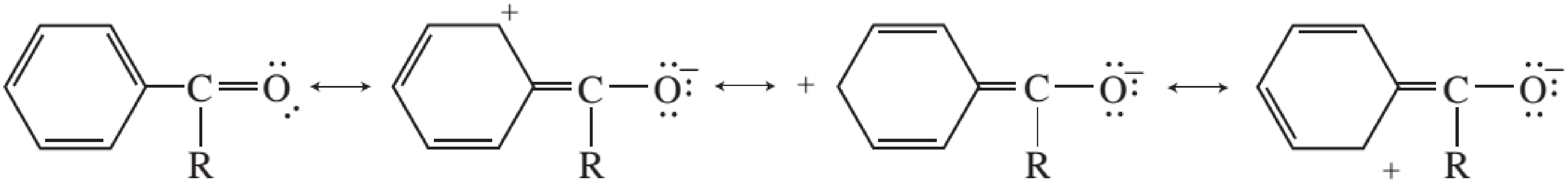
\+ For anilinium ion, the primary and secondary bands do not shift at all (*the spectrum of anilinium ion is almost identical to that of benzene*).

➢ The quaternary nitrogen of anilinium ion has no unshared pairs of electrons to interact with the benzene π system.

AROMATIC COMPOUNDS: Substituents Capable of π-Conjugation

- ➢ As in the case of *n* electrons, interaction of the benzene-ring electrons and the π electrons of the substituent can produce a new electron transfer band.

- ➢ This new band may be so intense as to obscure the secondary band of the benzene system.



- ➢ In the case of benzoic acid, the primary and secondary bands are shifted substantially from those noted for benzene.

Electron-Releasing and Electron-Withdrawing Effects

- Substituents have differing effects on the positions of absorption maxima, depending on whether they are electron releasing or electron withdrawing.

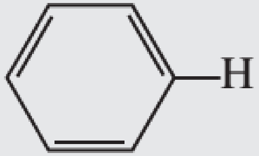
+ Any substituent, regardless of its influence on the electron distribution in the aromatic molecule, shifts the primary absorption band to longer wavelength.

+ Electron-withdrawing groups have essentially NO effect on the position of the secondary absorption band.

+ **Electron-releasing** groups **increase** both the **wavelength** and the **intensity** of the **secondary** absorption band.

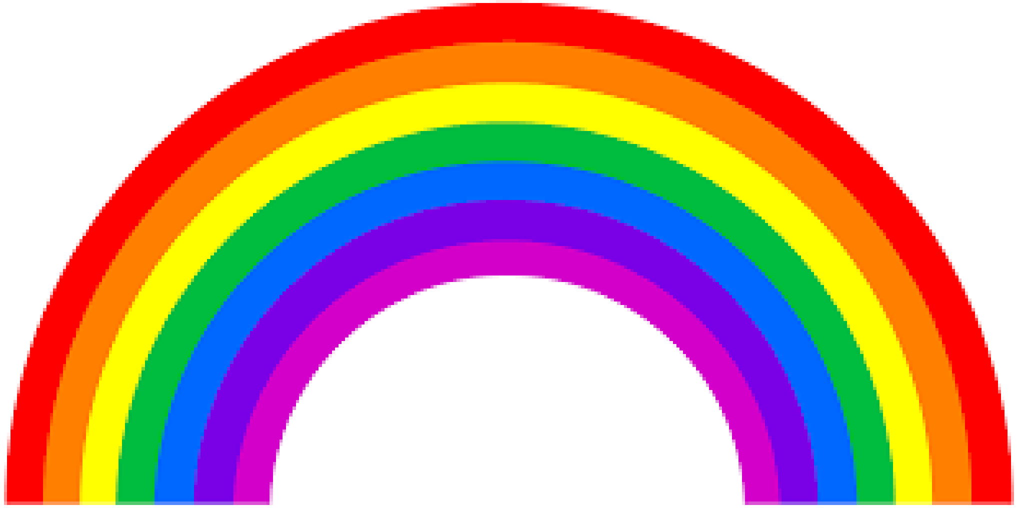
Electron-releasing and Electron-withdrawing Effects

ULTRAVIOLET MAXIMA FOR VARIOUS AROMATIC COMPOUNDS

		Primary		*Secondary*	
Substituent		λ (nm)	ε	λ (nm)	ε
		203.5	7,400	254	204
Electron-releasing substituents	$-CH_3$	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
	$-OCH_3$	217	6,400	269	1,480
	$-NH_2$	230	8,600	280	1,430
Electron-withdrawing substituents	$-CN$	224	13,000	271	1,000
	$-COOH$	230	11,600	273	970
	$-COCH_3$	245.5	9,800		
	$-CHO$	249.5	11,400		
	$-NO_2$	268.5	7,800		

VISIBLE SPECTRA: COLORS IN COMPOUNDS

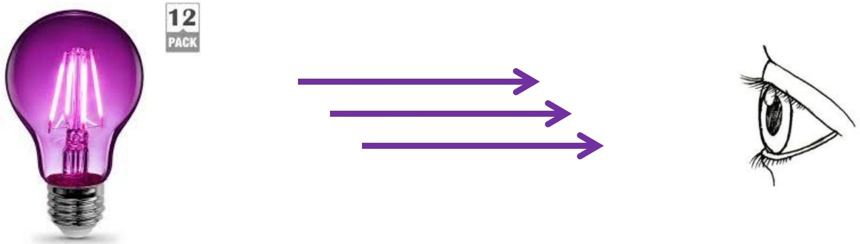
- Light waves with wavelengths between **400 nm and 800 nm** (**visible** region) appear colored to the human eye.
- Light from the sun is white light, like the light from normal light bub.
- As can be seen in light diffraction by a prism or in a rainbow - *light diffracted by small water drops as prisms* - one end of the visible spectrum is violet, and the other is red.
- Light with wavelengths **near 400 nm is violet**, while that with wavelengths **near 800 nm is red.**



VISIBLE SPECTRA: COLOR IN COMPOUNDS

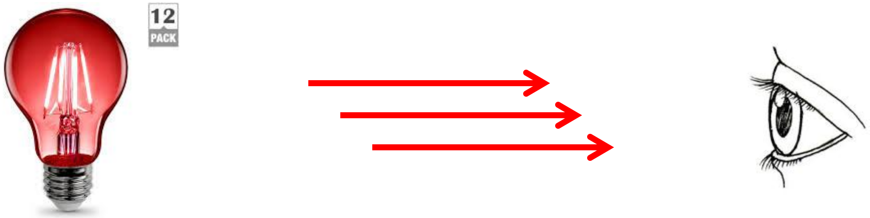
- When we observe light **emitted from a source**, as from a lamp or from the sun, we observe the **color** corresponding to the wavelength **of the light being emitted**.

+ A light source emitting violet light emits light at the high-energy end of the visible spectrum.



Violet light bulb

+ A light source emitting red light emits light at the low-energy end of the spectrum.

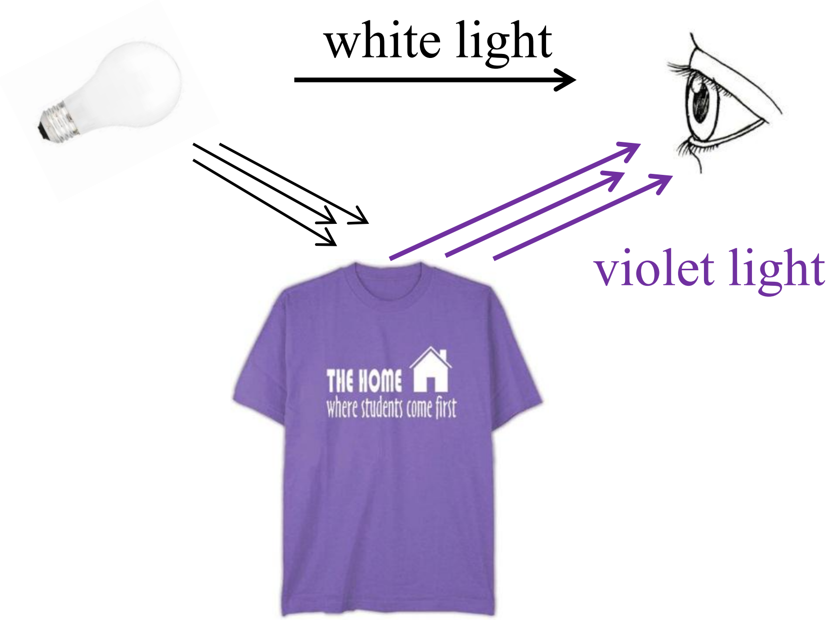


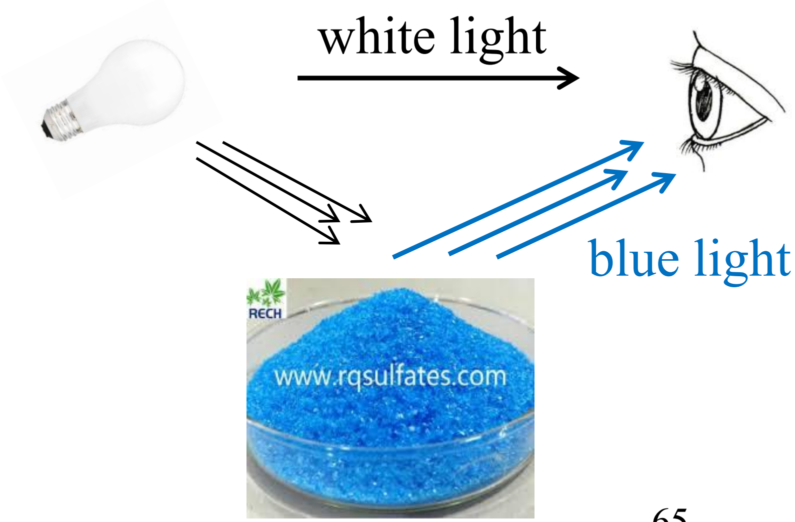
VISIBLE SPECTRA: COLOR IN COMPOUNDS

➢ When we observe the color of an **object or a substance**, we do not observe that object or substance emitting light. Rather, we observe the light that is being **reflected**.

+ The color that our eye perceives is not the color corresponding to the wavelength of the light absorbed but its **complement**.

+ When white light falls on an object, light of a particular wavelength is absorbed. The remainder of the light is reflected to reach the eye. The eye and brain register **ALL** of the reflected light waves as the color *complementary* to the color that was absorbed.





VISIBLE SPECTRA: COLOR IN COMPOUNDS

➢ When we observe the color of an **object or a substance**, we do not observe that object or substance emitting light. Rather, we observe the light that is being **reflected**.

+ The color that our eye perceives is not the color corresponding to the wavelength of the light absorbed but its **complement**.

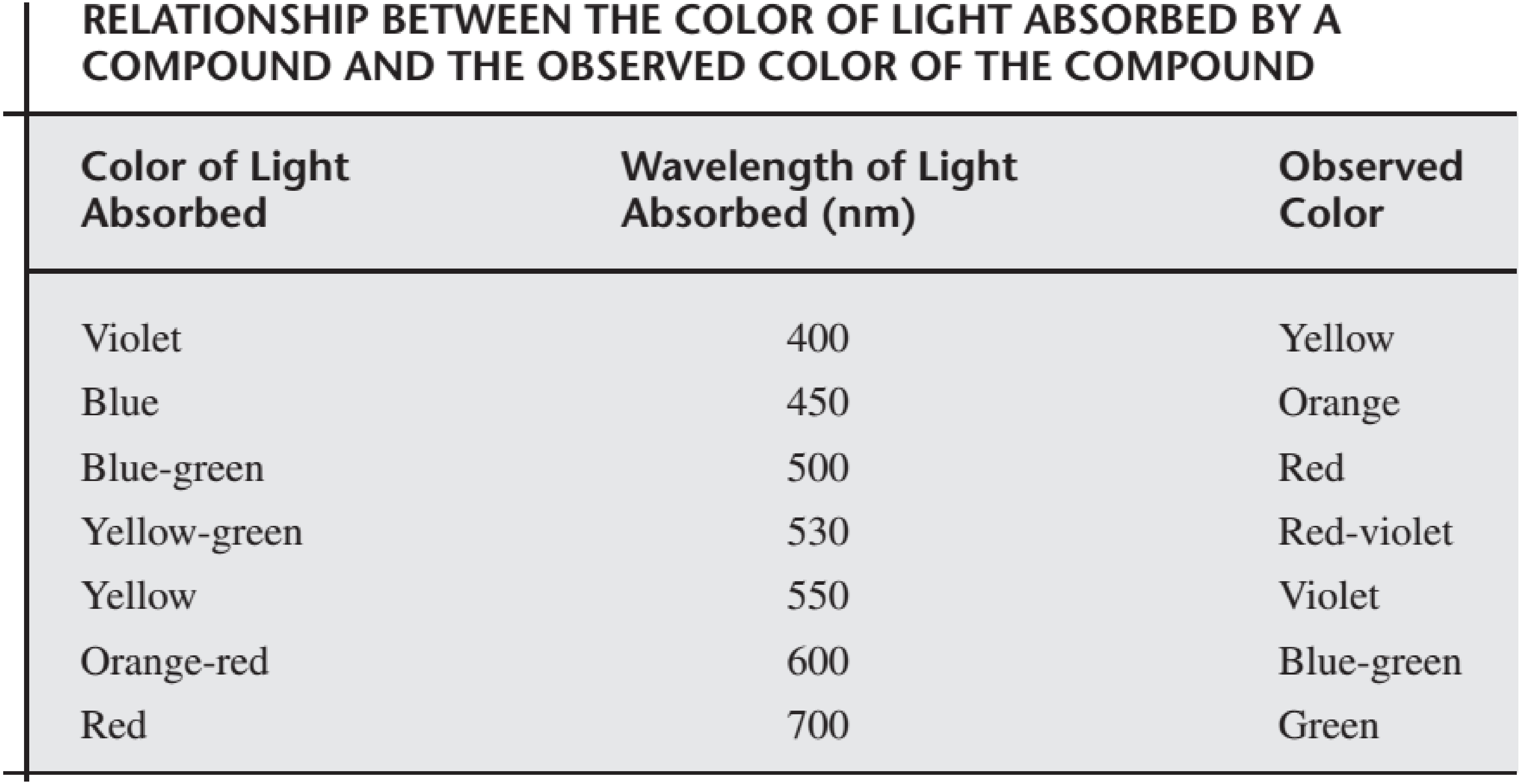
+ When white light falls on an object, light of a particular wavelength is absorbed. The remainder of the light is reflected to reach the eye. The eye and brain register **ALL** of the reflected light waves as the color *complementary* to the color that was absorbed.

+ In the case of transparent objects or solutions, the eye receives the light that is **transmitted**.

+ Any light (of a certain wave length) and its complementary light combine to produce white light).

VISIBLE SPECTRA: COLOR IN COMPOUNDS

- This table illustrates the relationship between the wavelength of light absorbed by a substance and the color perceived by an observer.



RELATIONSHIP BETWEEN THE COLOR OF LIGHT ABSORBED BY A COMPOUND AND THE OBSERVED COLOR OF THE COMPOUND

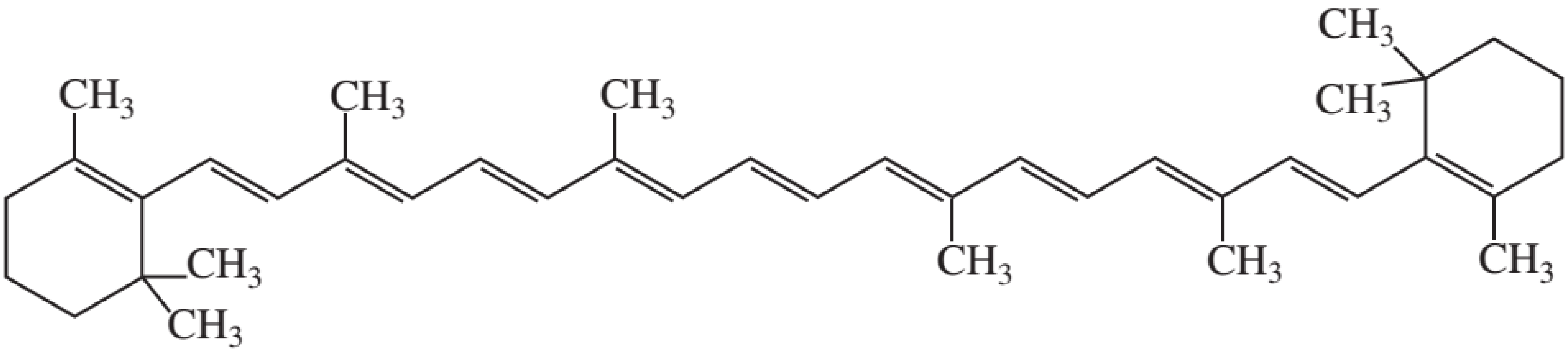
Color of Light Absorbed	Wavelength of Light Absorbed (nm)	Observed Color
Violet	400	Yellow
Blue	450	Orange
Blue-green	500	Red
Yellow-green	530	Red-violet
Yellow	550	Violet
Orange-red	600	Blue-green
Red	700	Green

Bảng 3.2- Quan hệ giữa tia bị hấp thụ và màu của chất hấp thụ

[illegible]
xanh

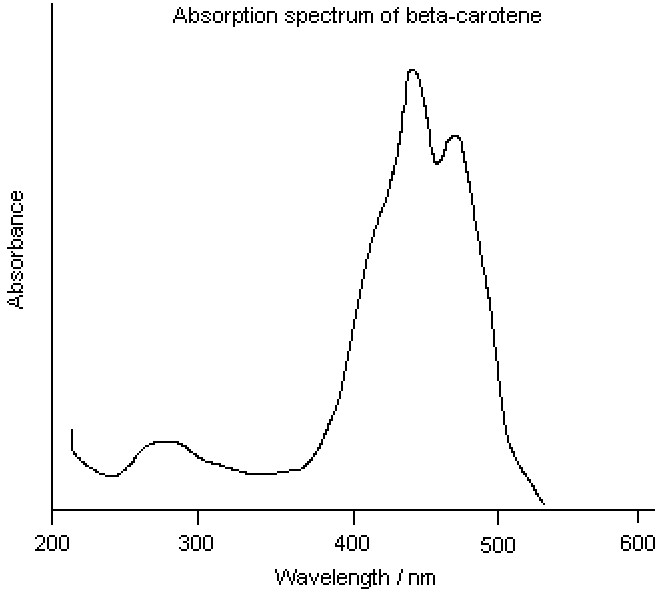
Tia bị hấp thụ		Màu của chất hấp thụ
λ, nm	màu	(màu của tia còn lại)
400 - 430	tím	vàng lục
430 - 490	xanh	vàng da cam
490 - 510	lục xanh	đỏ
510 - 530	lục	đỏ tía
530 - 560	lục vàng	tím
560 - 590	vàng	xanh
590 - 610	da cam	xanh lục
610 - 730	đỏ	lục

VISIBLE SPECTRA: COLOR IN COMPOUNDS

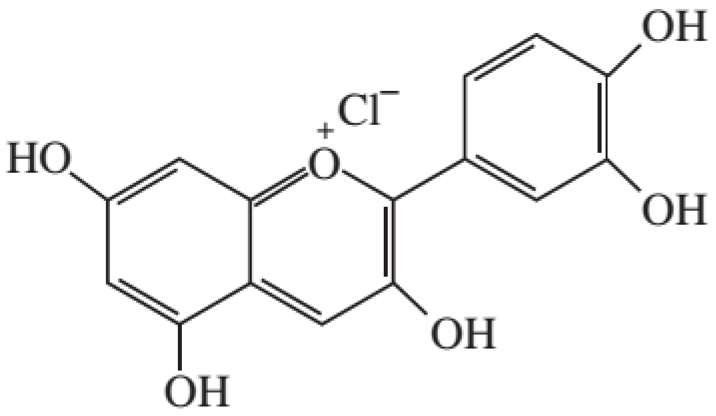


β-Carotene (a carotenoid, which is a class of plant pigments)

$$\lambda_{max} = 452 \text{ nm}$$



VISIBLE SPECTRA: COLOR IN COMPOUNDS



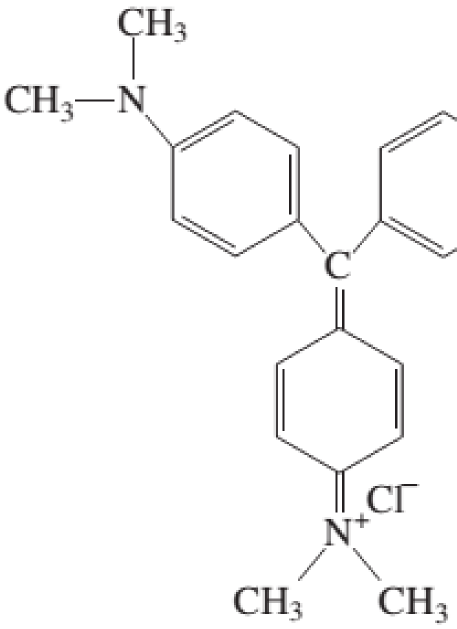
Cyanidin (blue pigment of cornflower):

λmax = 545 nm,

blue

Blue cornflower pigment

VISIBLE SPECTRA: COLOR IN COMPOUNDS



Malachite green (a triphenylmethane dye)
$\lambda_{max} = 617$ nm

Green

WHAT TO LOOK FOR IN AN ULTRAVIOLET SPECTRUM

1. *A single band of* ***low-to-medium*** *intensity (ε = 100 to 10.000) at wavelengths less than* ***220 nm*** usually indicates an ***n*** **→ σ*** transition.
+ Amines, alcohols, ethers, and thiols are possibilities, provided the nonbonded electrons are **NOT** included in a conjugated system.

2. *A single band of* ***low*** *intensity (ε = 10 to 100) in the region* ***250 to 360 nm****, with no major absorption at shorter wavelengths (200 to 250 nm)*, usually indicates an ***n*** **→ π*** transition.

+ Since the absorption does **NOT** occur at long wavelength, a **simple, or unconjugated, chromophore** is indicated, generally one that contains an O, N, or S atom.

+ Examples: C=O, C=N, N=N, -NO_2, -COOR, -COOH, or -$CONH_2$.

WHAT TO LOOK FOR IN AN ULTRAVIOLET SPECTRUM

3. ***Two** bands of **medium** intensity (**ε = 1,000 to 10,000**), both with* λ_{max} ***above 200 nm***, generally indicate the presence of an **aromatic** system.

\+ Substitution on the aromatic rings increases the molar absorptivity above 10.000, particularly if the substituent increases the length of the conjugated system.

4. *Bands of **high intensity** (**ε = 10.000 to 20.000**) that appear **above 210 nm*** generally represent either an ***α,β*-unsaturated ketone**, a diene, or a polyene.

\+ The greater the length of the conjugated system, the longer the observed wavelength.

\+ For dienes, the λ_{max} may be calculated using the Woodward–Fieser rules.

WHAT TO LOOK FOR IN AN ULTRAVIOLET SPECTRUM

5. *Simple ketones, acids, esters, amides, and other compounds containing both π systems and unshared electron pairs show* ***two*** *absorptions:* an ***n* → π*** transition at longer wavelengths (>300 nm, low intensity) and a **π → π*** transition at shorter wavelengths (<250 nm, high intensity).

+ With conjugation (enones), the λ_{max} of the π → π* band moves to longer wavelengths and can be predicted by Woodward's rules.

+ The ε value usually rises above 10.000. As it is very intense, it may obscure or bury the weaker *n* → π* transition.

+ For *α,β*-unsaturated esters and acids, Nielsen's rules may be used to predict the position of λ_{max}.

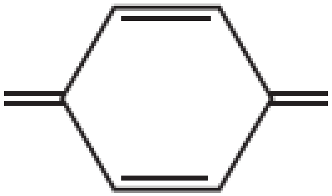
WHAT TO LOOK FOR IN AN ULTRAVIOLET SPECTRUM

6. *Compounds that are highly colored* (have absorption in the visible region) are likely to contain a long-chain conjugated system or a polycyclic aromatic chromophore.

+ Benzenoid compounds may be colored if they have enough conjugating substituents.

+ For non-aromatic systems, usually a minimum of **four to five** conjugated chromophores are required to produce absorption in the visible region.

+ Some simple nitro, azo, nitroso, α-diketo, polybromo, and polyiodo compounds may also exhibit color, as may many compounds with quinoid structures.



EXERCISES

***1.** The ultraviolet spectrum of benzonitrile shows a primary absorption band at 224 nm and a secondary band at 271 nm.

(a) If a solution of benzonitrile in water, with a concentration of 1×10^{-4} molar, is examined at a wavelength of 224 nm, the absorbance is determined to be 1.30. The cell length is 1 cm. What is the molar absorptivity of this absorption band?

(b) If the same solution is examined at 271 nm, what will be the absorbance reading ($\varepsilon = 1000$)? What will be the intensity ratio, I_0/I?

1. (a) $\varepsilon = 13{,}000$

(b) $I_0/I = 1.26$

*__4.__ The UV spectrum of acetone shows absorption maxima at 166, 189, and 279 nm. What type of transition is responsible for each of these bands?

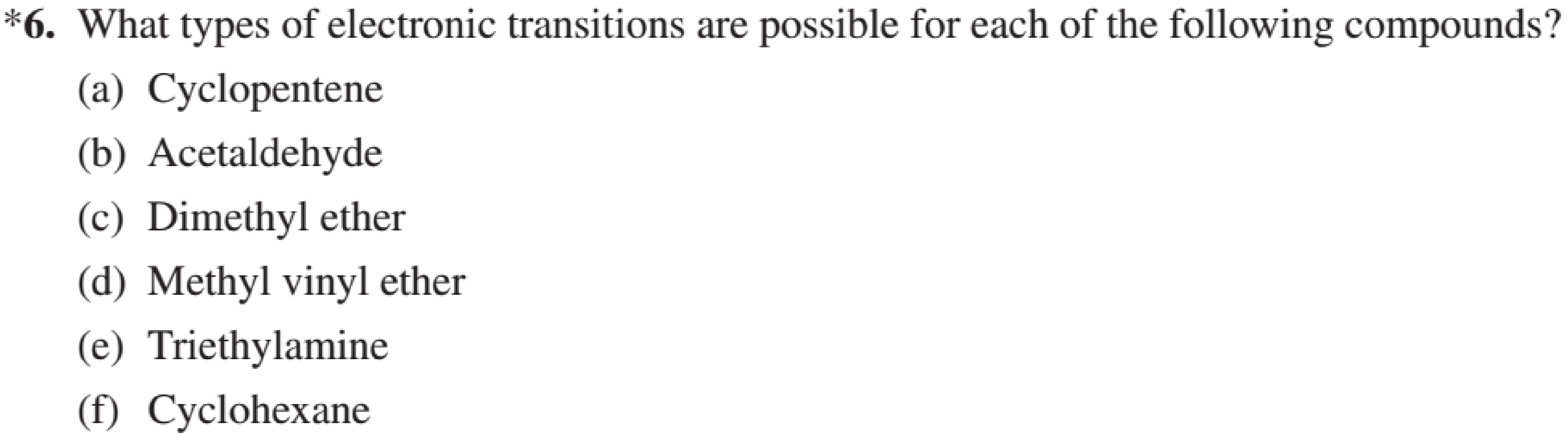
4. 166 nm: $n \rightarrow \sigma^*$
   189 nm: $\pi \rightarrow \pi^*$
   279 nm: $n \rightarrow \pi^*$

VISIBLE SPECTRA: COLOR IN COMPOUNDS

*__5.__ Chloromethane has an absorption maximum at 172 nm, bromomethane shows an absorption at 204 nm, and iodomethane shows a band at 258 nm. What type of transition is responsible for each band? How can the trend of absorptions be explained?

5. Each absorption is due to $n \rightarrow \sigma^*$ transitions. As one goes from the *chloro* to the *bromo* to the *iodo* group, the electronegativity of the halogens decreases. The orbitals interact to different degrees, and the energies of the n and the σ^* states differ.

VISIBLE SPECTRA: COLOR IN COMPOUNDS

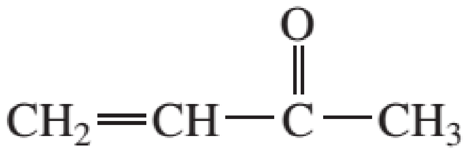


*6. What types of electronic transitions are possible for each of the following compounds?

- (a) Cyclopentene
- (b) Acetaldehyde
- (c) Dimethyl ether
- (d) Methyl vinyl ether
- (e) Triethylamine
- (f) Cyclohexane

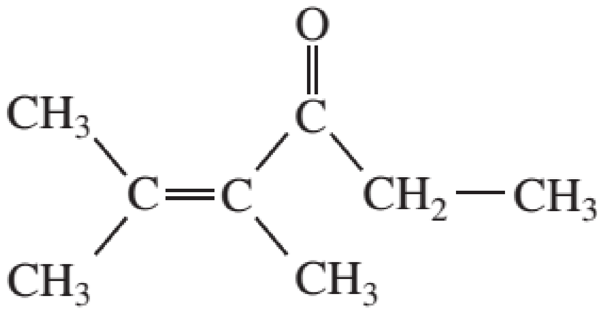
*3. Predict the UV maximum for each of the following substances:

(a)

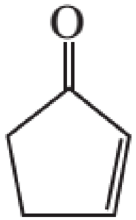


$CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}CH_3$

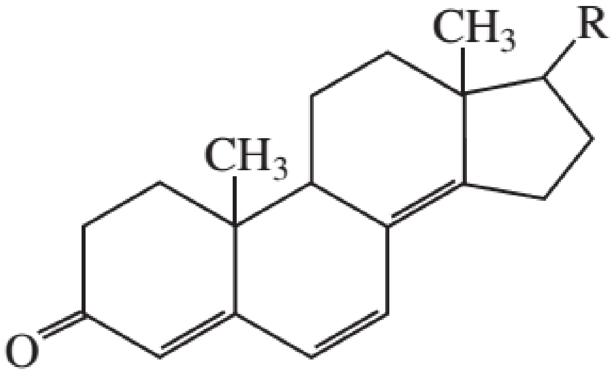
(b)



(c)



(d)



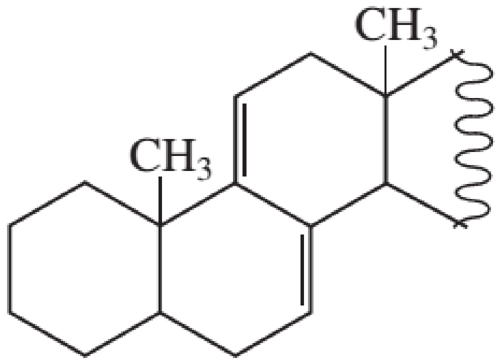
3. (a) Calculated: 215 nm observed: 213 nm

(b) Calculated: 249 nm observed: 249 nm

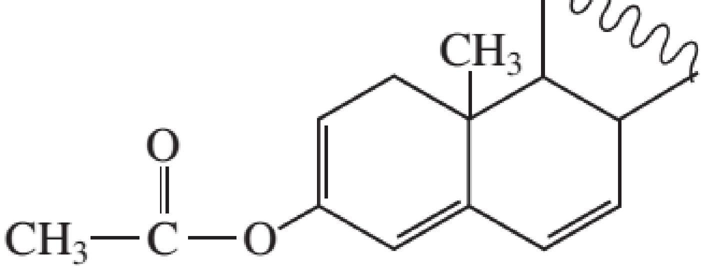
(c) Calculated: 214 nm observed: 218 nm

(d) Calculated: 356 nm observed: 348 nm

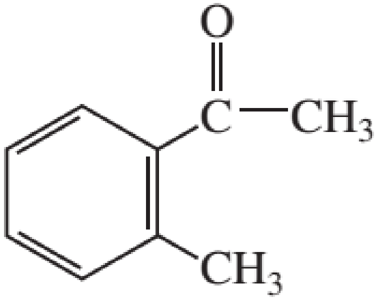
(e)



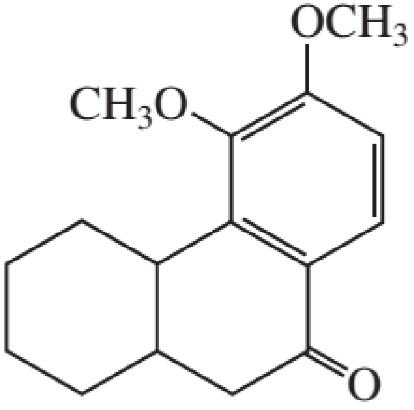
(f)



(g)



(h)



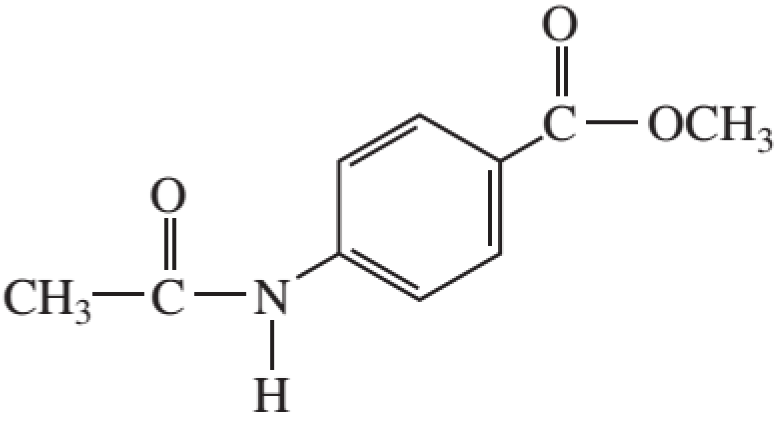
(e) Calculated: 244 nm observed: 245 nm

(f) Calculated: 303 nm observed: 306 nm

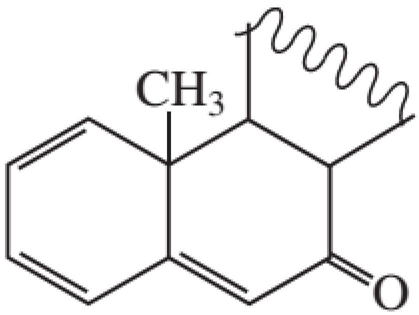
(g) Calculated: 249 nm observed: 245 nm

(h) Calculated: 281 nm observed: 278 nm

(i)



(j)

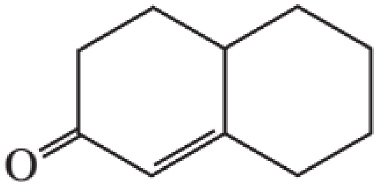


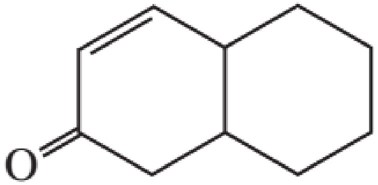
(i) Calculated: 275 nm observed: 274 nm

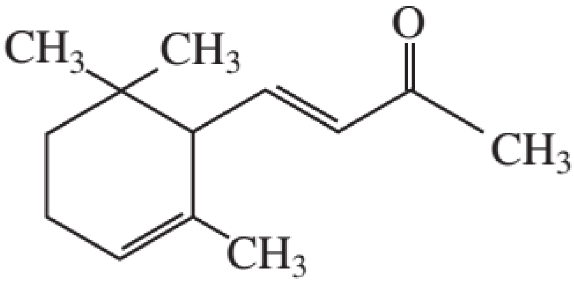
(j) Calculated: 349 nm observed: 348 nm

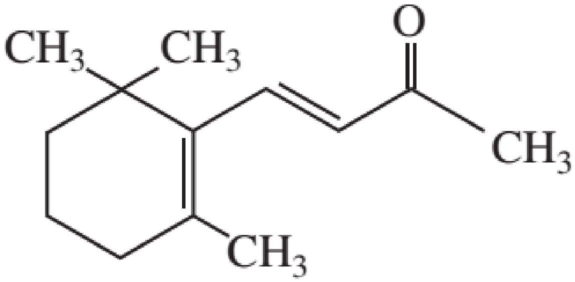
VISIBLE SPECTRA: COLOR IN COMPOUNDS

7. Predict and explain whether UV/visible spectroscopy can be used to distinguish between the following pairs of compounds. If possible, support your answers with calculations.

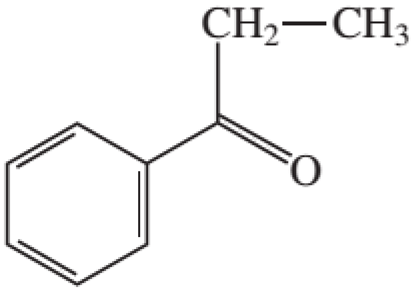


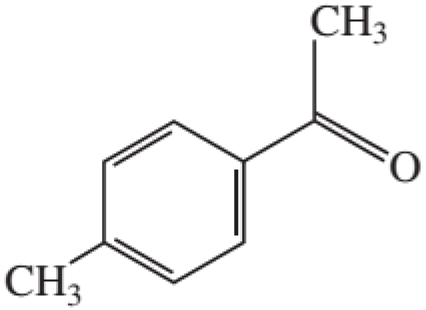


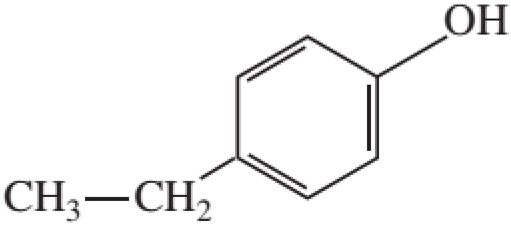


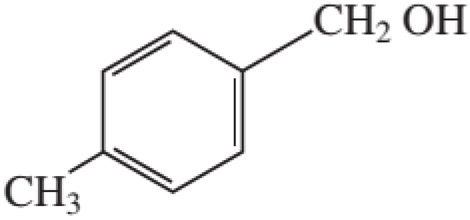


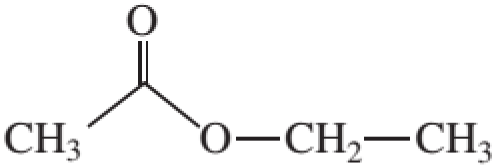
VISIBLE SPECTRA: COLOR IN COMPOUNDS

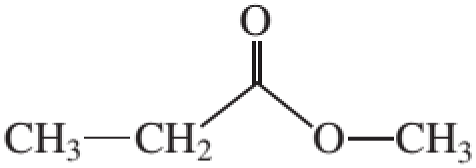




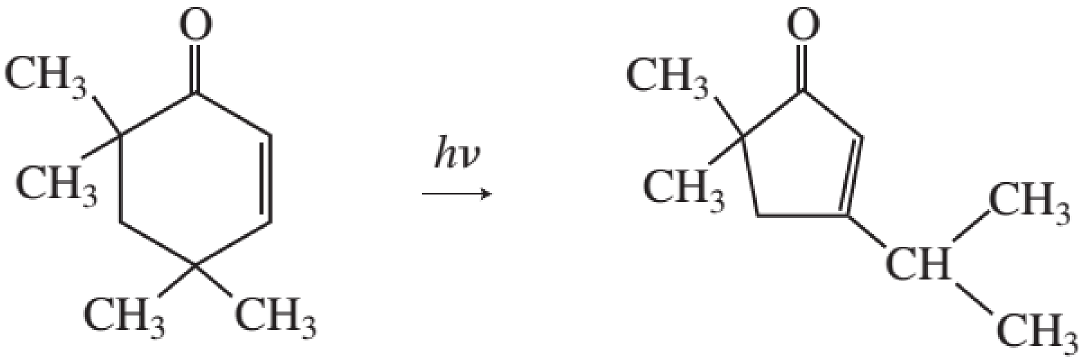








8. (a) Predict the UV maximum for the reactant and product of the following photochemical reaction:



(b) Is UV spectroscopy a good way to distinguish the reactant from the product?

(c) How would you use infrared spectroscopy to distinguish between the reactant and the product?

(d) How would you use proton NMR to distinguish between the reactant and the product (two ways)?

(e) How could you distinguish between the reactant and the product by using DEPT NMR (see Chapter 9)?

***2.** Draw structural formulas that are consistent with the following observations:

(a) An acid $C_7H_4O_2Cl_2$ shows a UV maximum at 242 nm.

(b) A ketone $C_8H_{14}O$ shows a UV maximum at 248 nm.

(c) An aldehyde $C_8H_{12}O$ absorbs in the UV with $\lambda_{max} = 244$ nm.

2. (a) 2,4-Dichlorobenzoic acid or 3,4-dichlorobenzoic acid

(b) 4,5-Dimethyl-4-hexen-3-one

(c) 2-Methyl-1-cyclohexenecarboxaldehyde