

Chapter 14

Application of Ultraviolet/Visible Molecular Absorption Spectrometry

Absorption measurements based upon ultraviolet and visible radiation find widespread application for the identification and determination of myriad inorganic and organic species. Molecular ultraviolet/visible absorption methods are perhaps the most widely used of all **quantitative** analysis techniques in chemical and clinical laboratories throughout the world.

Absorptivity (a or ϵ)

Defines how much radiation will be absorbed by a molecule at a given concentration and wavelength

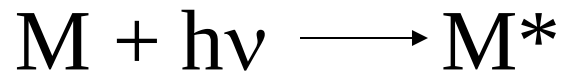
- Is termed molar absorptivity (ϵ) if concentration is expressed in molarity (M, mol/L)
- Can be calculated using Beer's Law ($A = abc = \epsilon bc$)
- If units of b is cm and c is M then ϵ is $M^{-1}cm^{-1}$ or $Lmol^{-1}cm^{-1}$
- Magnitude of ϵ is an indication of the probability of the electronic transition

The magnitude of Molar Absorptivities

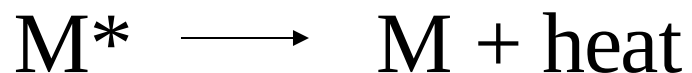
Molar absorptivities range from zero up to a maximum on the order of 10^5 are observed. The magnitude of ϵ depends upon the probability for an energy-absorbing transition to occur. Peaks having molar absorptivities less than about 10^3 are classified as being of low intensity. They result from so-called forbidden transitions, which have probabilities of occurrence that are less than 0.01.

ABSORBING SPECIES

The absorption of ultraviolet or visible radiation by a molecular species M can be considered to be a two-step process, excitation



The lifetime of the excited species is brief (10^{-8} to 10^{-9} s). Relaxation involves conversion of the excitation energy to heat.



The absorption of ultraviolet or visible radiation generally results from excitation of bonding electrons.

Electronic Transitions

There are three types of electronic transitions. The three include transitions involving:

- (1) π , σ , and n electrons
- (2) d and f electrons
- (3) charge transfer electrons.

Types of Absorbing Electrons

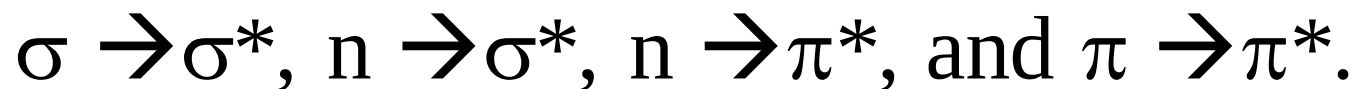
The electrons that contribute to absorption by a molecule are: (1) those that participate directly in **bond formation between atoms**; (2) **nonbonding** or unshared outer electrons that are largely localized about such atoms as **oxygen, the halogens, sulfur, and nitrogen**. The molecular orbitals associated with single bonds are designated as sigma (σ) orbitals, and the corresponding electrons are σ electrons.

Types of Absorbing Electrons

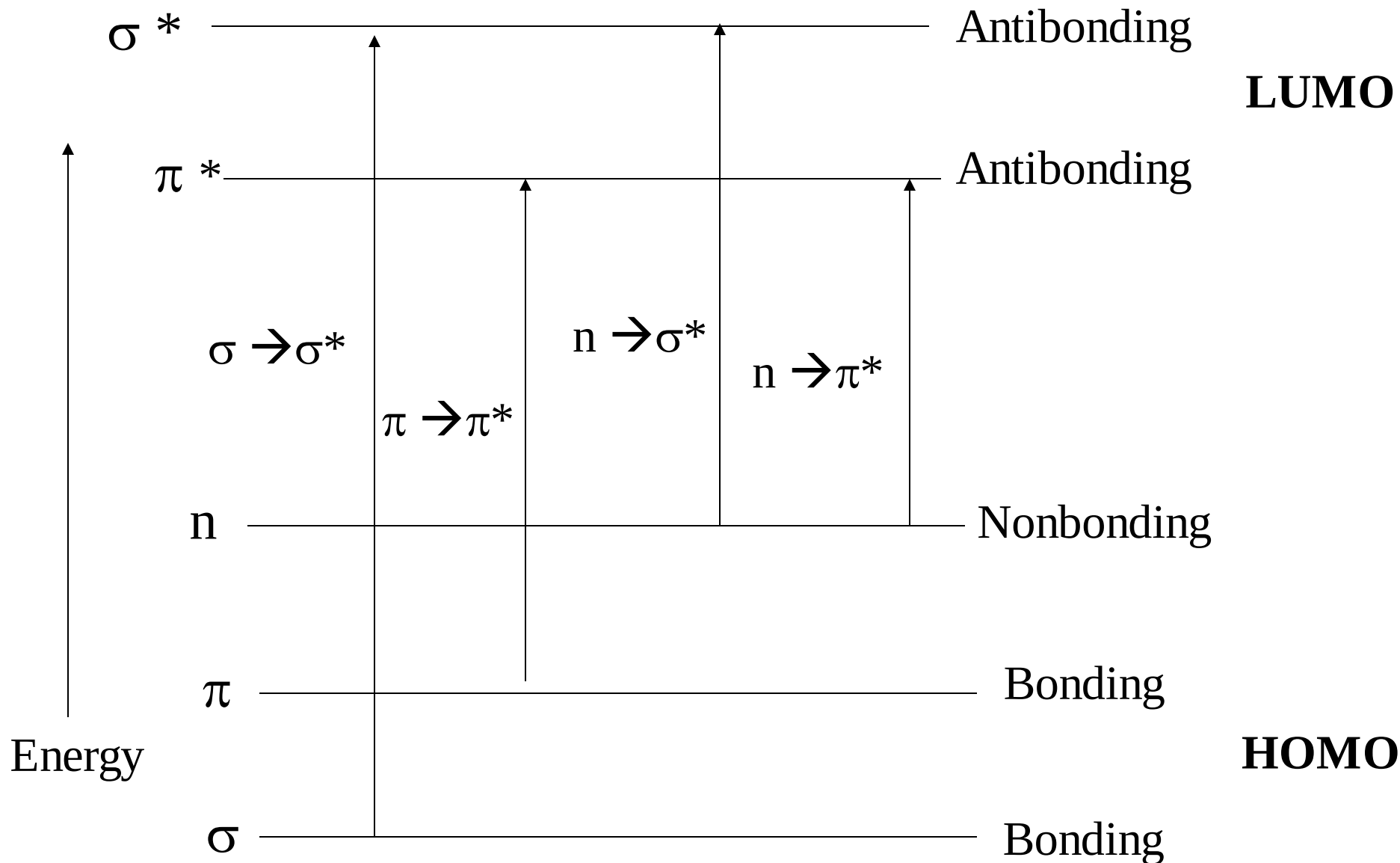
The double bond in a molecule contains two types of molecular orbitals: a sigma (σ) orbital and a pi (π) molecular orbital. Pi orbitals are formed by the parallel overlap of atomic p orbitals. In addition to σ and π electrons, many compounds contain nonbonding electrons. These unshared electrons are designated by the symbol n.

Energy

The energies for the various types of molecular orbitals differ significantly. The energy level of a nonbonding electron lies between the energy levels of the bonding and the antibonding π and σ orbitals. Electronic transitions among certain of the energy levels can be brought about by the absorption of radiation. Four types of transitions are possible:



LUMO: lowest unoccupied molecular orbital



HOMO: highest occupied molecular orbital

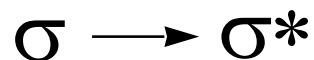
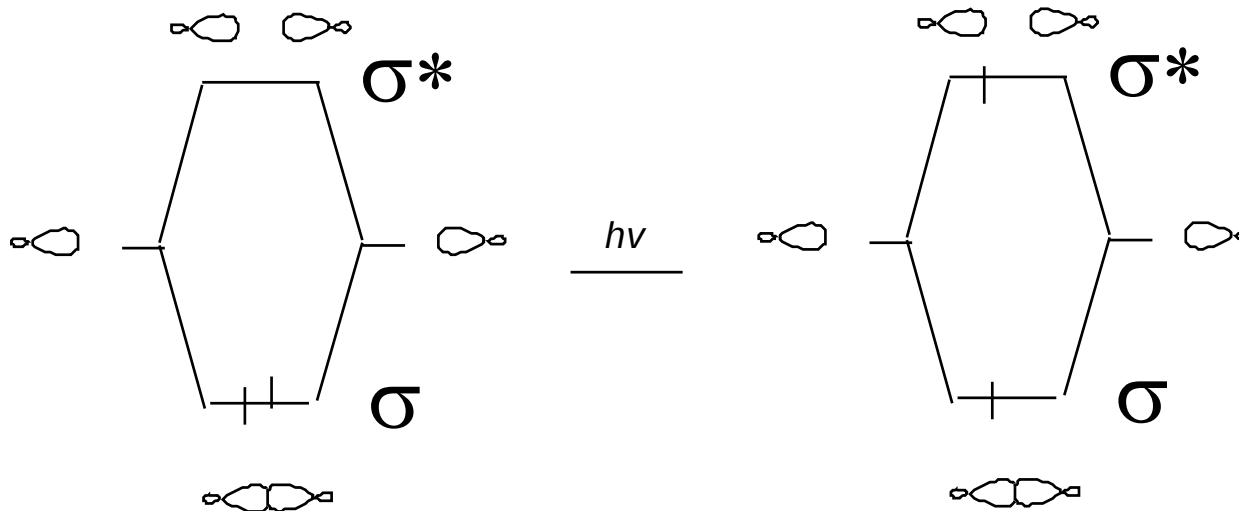
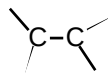
For convenience of reference, definitions of the various spectral regions have been set by the Joint Committee on Nomenclature in Applied Spectroscopy:

Region	Wavelength (nm)
Far ultraviolet	10-200
Near ultraviolet	200-380
Visible	380-780
Near infrared	780-3000
Middle infrared	3000-30,000
Far infrared	30,000-300,000
Microwave	300,000-1,000,000,000

$\sigma \rightarrow \sigma^*$ Transition

An electron in a bonding σ orbital of a molecule is excited to the corresponding antibonding orbital by the absorption of radiation. The energy required to induce a $\sigma \rightarrow \sigma^*$ transition is large. Methane (CH_4) can undergo only $\sigma \rightarrow \sigma^*$ transitions, exhibits an absorption maximum λ_{max} at 125 nm. Absorption maxima due to $\sigma \rightarrow \sigma^*$ transitions are never observed in the ordinarily accessible ultraviolet region (Far UV range).

Ethane

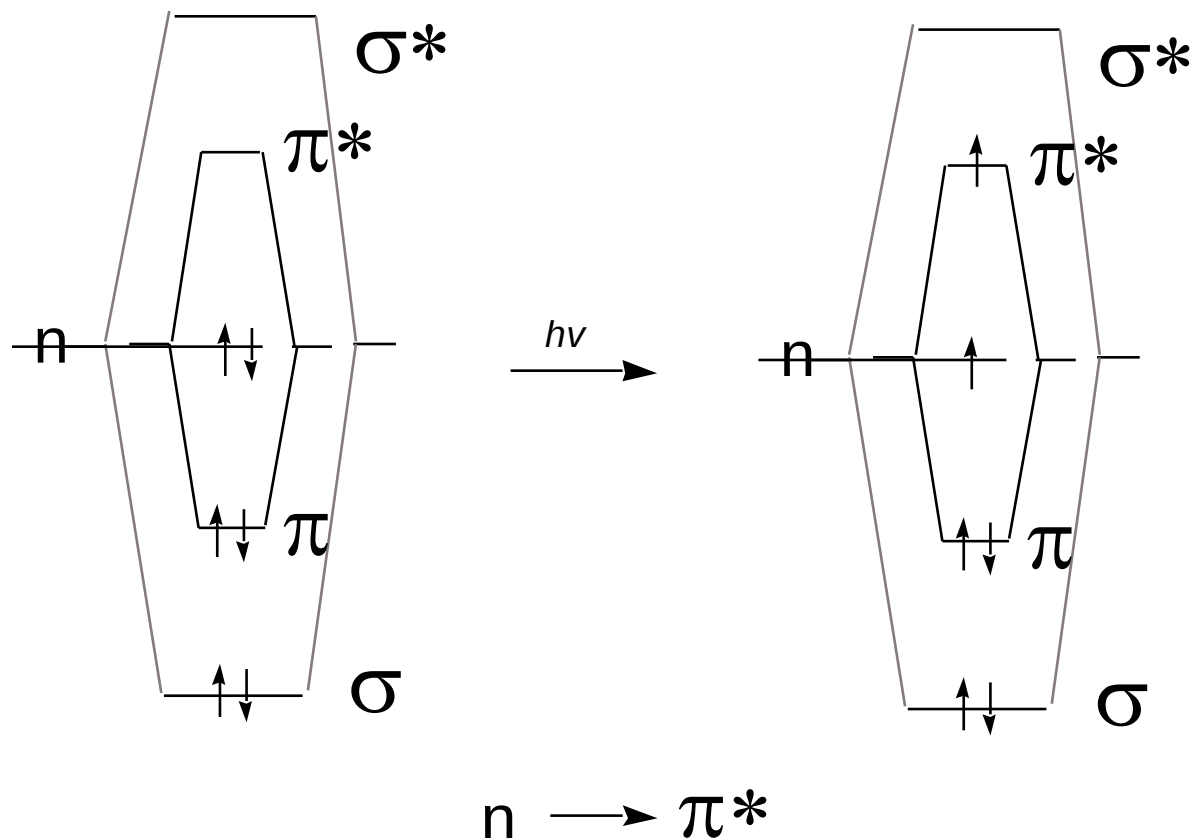
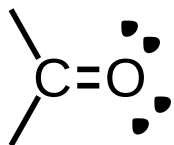


$$\lambda_{\max} = 135 \text{ nm} \quad (\text{a high energy transition})$$

Absorptions having $\lambda_{\max} < 200 \text{ nm}$ are difficult to observe because everything (including quartz glass and air) absorbs in this spectral region.

$n \rightarrow \sigma^*$ Transitions

Saturated compounds containing atoms with unshared electrons are capable of $n \rightarrow \sigma^*$ transitions. These transitions require less energy than the $\sigma \rightarrow \sigma^*$ type and can be brought about by radiation in the region of between 150 and 250 nm, with most absorption peaks appearing below 200 nm. The molar absorptivities are low to intermediate in magnitude and range between 100 and 3000 L cm⁻¹ mol⁻¹.



The n to π^* transition is at even **lower wavelengths** but is not as strong as π to π^* transitions. It is said to be “forbidden.”

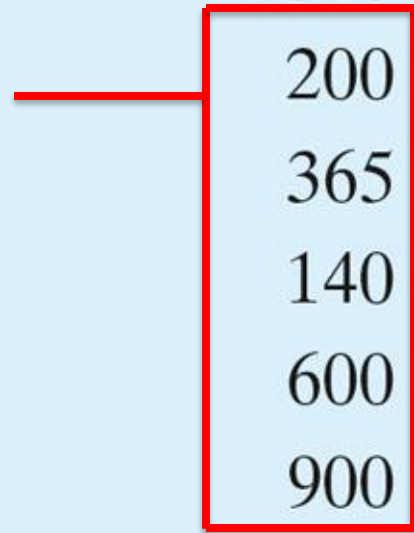
Example:

Acetone: $\pi \rightarrow \pi^*$ $\lambda_{\max} = 188 \text{ nm}$; $\epsilon = 1860$
 $n \rightarrow \pi^*$ $\lambda_{\max} = 279 \text{ nm}$; $\epsilon = 15$

TABLE 14-2 Absorption by Organic Compounds Containing Heteroatoms with Nonbonding Electrons

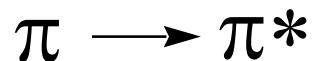
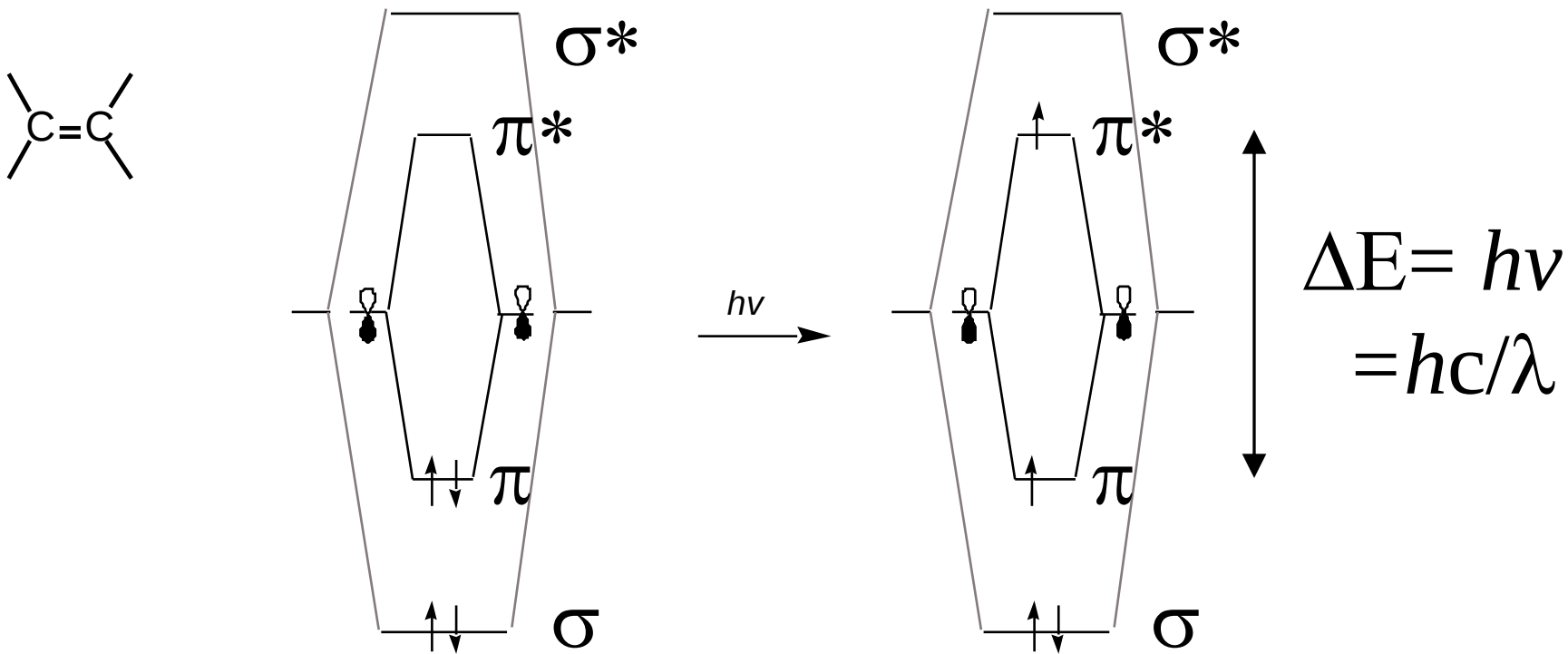
Compound	λ_{max} , nm	ϵ_{max}
CH ₃ OH	167	1480
(CH ₃) ₂ O	184	2520
CH ₃ Cl	173	200
CH ₃ I	258	365
(CH ₃) ₂ S	229	140
CH ₃ NH ₂	215	600
(CH ₃) ₃ N	227	900

LOW!



$n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ Transitions

Most applications of absorption spectroscopy are based upon transitions for n or π electrons to the π^* excited state because the energies required for these processes bring the absorption peaks into an experimentally convenient spectral region (200 to 780 nm). Both transitions require the presence of an unsaturated functional group to provide the π orbitals. The molar absorptivities for peaks associated with excitation to the n, π^* state are generally low and ordinarily range from 10 and 100 $\text{L cm}^{-1} \text{ mol}^{-1}$; values for $\pi \rightarrow \pi^*$ transitions are normally take place in the range between 1000 and 10,000.



Example: ethylene absorbs at longer wavelengths:

$$\lambda_{\text{max}} = 185 \text{ nm } \epsilon = 10,000$$

TABLE 14-1 Absorption Characteristics of Some Common Chromophores

Chromophore	Example	Solvent	$\lambda_{\max}$, nm	$\epsilon_{\max}$	Transition Type
Alkene	$\text{C}_6\text{H}_{13}\text{CH}=\text{CH}_2$	<i>n</i> -Heptane	177	13,000	$\pi \rightarrow \pi^*$
Alkyne	$\text{C}_5\text{H}_{11}\text{C}\equiv\text{C}-\text{CH}_3$	<i>n</i> -Heptane	178	10,000	$\pi \rightarrow \pi^*$
			196	2000	—
			225	160	—
Carbonyl	$\text{CH}_3\text{C}(=\text{O})\text{CH}_3$	<i>n</i> -Hexane	186	1000	$n \rightarrow \sigma^*$
			280	16	$n \rightarrow \pi^*$
	$\text{CH}_3\text{CH}=\text{O}$	<i>n</i> -Hexane	180	large	$n \rightarrow \sigma^*$
			293	12	$n \rightarrow \pi^*$
Carboxyl	CH_3COOH	Ethanol	204	41	$n \rightarrow \pi^*$
Amido	$\text{CH}_3\text{C}(=\text{O})\text{NH}_2$	Water	214	60	$n \rightarrow \pi^*$
Azo	$\text{CH}_3\text{N}=\text{NCH}_3$	Ethanol	339	5	$n \rightarrow \pi^*$
Nitro	CH_3NO_2	Isooctane	280	22	$n \rightarrow \pi^*$
Nitroso	$\text{C}_4\text{H}_9\text{NO}$	Ethyl ether	300	100	—
			665	20	$n \rightarrow \pi^*$
Nitrate	$\text{C}_2\text{H}_5\text{ONO}_2$	Dioxane	270	12	$n \rightarrow \pi^*$

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Olefins and aromatics

$$\sigma \rightarrow \sigma^* < 185 \text{ nm}$$

$$n \rightarrow \sigma^* \text{ 150-250 nm}$$

$$\pi \rightarrow \pi^*$$

$$n \rightarrow \pi^* \text{ 200-700 nm}$$

Absorption by Organic Compounds

- All organic compounds are capable of absorbing electromagnetic radiation since all contain **valence electrons** that can be excited to higher energy levels
- The energies associated with electrons in single bonds are sufficiently high ($\sigma \rightarrow \sigma^*$) that absorption occurs in the Far-UV ($\lambda < 185$ nm). **Components of the atmosphere also absorb in this region.**
- This is the reason why normal **n-alkanes** organic compounds can be utilized as solvents in the UV/Vis region.
- Because of experimental difficulties association with the Far-ultraviolet region, most spectrophotometric investigations of organic compounds involves the longer wavelengths ($\lambda > 185$ nm)
- Most applications of Absorption spectroscopy are based on transitions for **$n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$. (UV/VIS 200-780nm)**
- Both $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ require the presence of unsaturated functional groups (double bonds) to provide the π orbitals. Molecule containing these functional groups are also referred to as “**chromophores**”

Absorption Definitions

Chromophore

A group of atoms that gives rise to electronic absorption

Or

A functional group capable of having characteristic electronic transitions is called a **chromophore** (color loving)

Or

The **chromophore** is a region in the molecule where the energy difference between two different molecular falls within the range of the visible spectrum

Auxochrome

A substituent that contains unshared electron pairs (OH, NH, X)

An auxochrome attached to a chromophore with π electrons shifts the λ_{max} to longer wavelengths

Common functional groups

Compound	$\lambda(\text{nm})$	Intensity/ ϵ	transition with lowest energy
CH_4	122	intense	$\sigma\text{-}\sigma^*(\text{C-H})$
CH_3CH_3	130	intense	$\sigma\text{-}\sigma^*(\text{C-C})$
CH_3OH	183	200	$\text{n-}\sigma^*(\text{C-O})$
CH_3SH	235	180	$\text{n-}\sigma^*(\text{C-S})$
CH_3NH_2	210	800	$\text{n-}\sigma^*(\text{C-N})$
CH_3Cl	173	200	$\text{n-}\sigma^*(\text{C-Cl})$
CH_3I	258	380	$\text{n-}\sigma^*(\text{C-I})$
$\text{CH}_2=\text{CH}_2$	165	16000	$\pi\text{-}\pi^*(\text{C=C})$
CH_3COCH_3	187	950	$\pi\text{-}\pi^*(\text{C=O})$
	273	14	$\text{n-}\pi^*(\text{C=O})$
CH_3CSCH_3	460	weak	$\text{n-}\pi^*(\text{C=S})$
$\text{CH}_3\text{N=NCH}_3$	347	15	$\text{n-}\pi^*(\text{N=N})$

Absorption Definitions

Bathochromic

A shift to longer wavelengths or red shift (increase in λ)

Hypsochromic

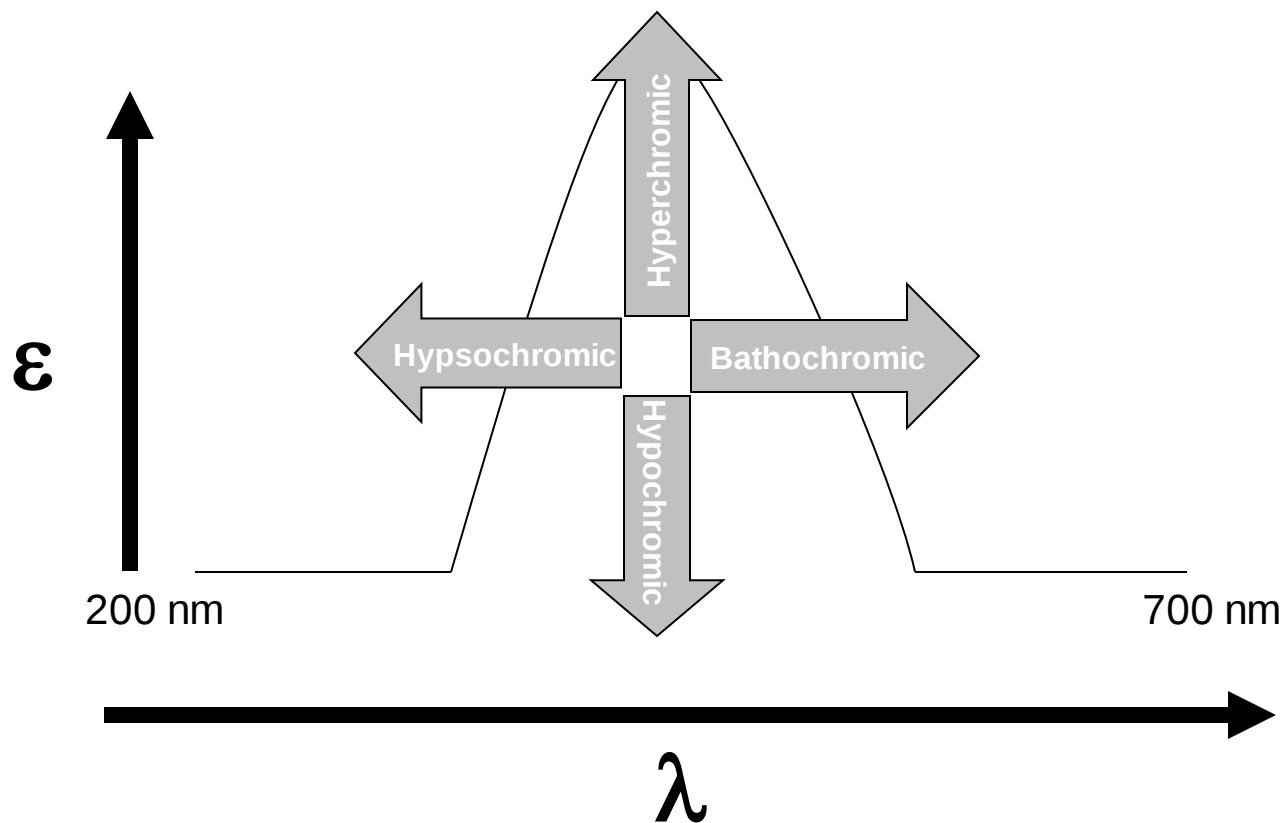
A shift to shorter wavelengths or blue shift (decrease in λ)

Hyperchromism

An increase in intensity of an absorption band (increase in ϵ_{max})

Hypochromism

A decrease in intensity of an absorption band (decrease in ϵ_{max})



Solvent Effects

A compound that contains both π and n electrons may exhibit **two absorption maxima** with change in solvent polarity

- $\pi \rightarrow \pi^*$ transitions absorb **~ 10** x more strongly than $n \rightarrow \pi^*$ transition
- $n \rightarrow \pi^*$ transition occur at **longer wavelengths** than $\pi \rightarrow \pi^*$
- Such a compound will exhibit two characteristic peaks in a nonpolar solvent such as hexane
- The two peaks will be shifted closer to each other in a polar and hydrogen bonding solvent such as ethanol

Solvent Effects

Molecules with absorption due to $\pi \rightarrow \pi^*$ transition exhibit **red shift** when dissolved in polar solvents as compared to nonpolar solvents

- Used to confirm the presence of $\pi \rightarrow \pi^*$ transitions in molecules

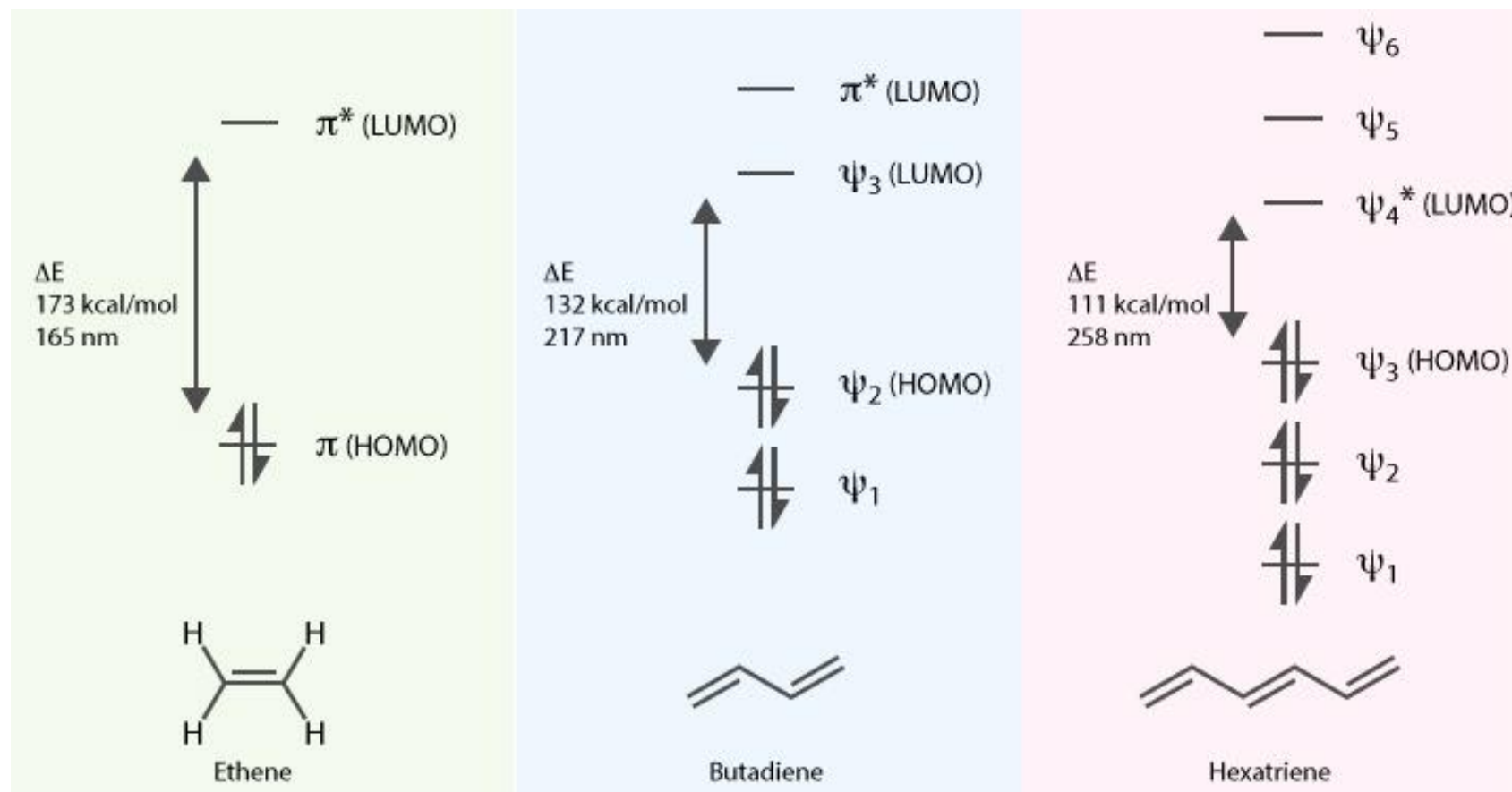
Molecules with absorption due to $n \rightarrow \pi^*$ transition exhibit **blue shift** when dissolved in solvents that are able to form hydrogen bonds

- Used to confirm the presence of n electrons in a molecule

Effect of Conjugation of Chromophores

π electrons are considered to be further delocalized by conjugation; the orbitals involve four (or more) atomic centers. The effect of this delocalization is to lower the energy level of the π^* orbital and give it less antibonding character. Absorption maxima are shifted to longer wavelengths as a consequence. Conjugation of chromophores, has a profound effect on spectral properties. 1,3-butadiene, $\text{CH}_2=\text{CHCH}=\text{CH}_2$, has a strong absorption band that is displaced to a longer wavelength by 20 nm compared with the corresponding peak for an unconjugated diene.

Effect of Conjugation of Chromophores



Effect of Conjugation of Chromophores

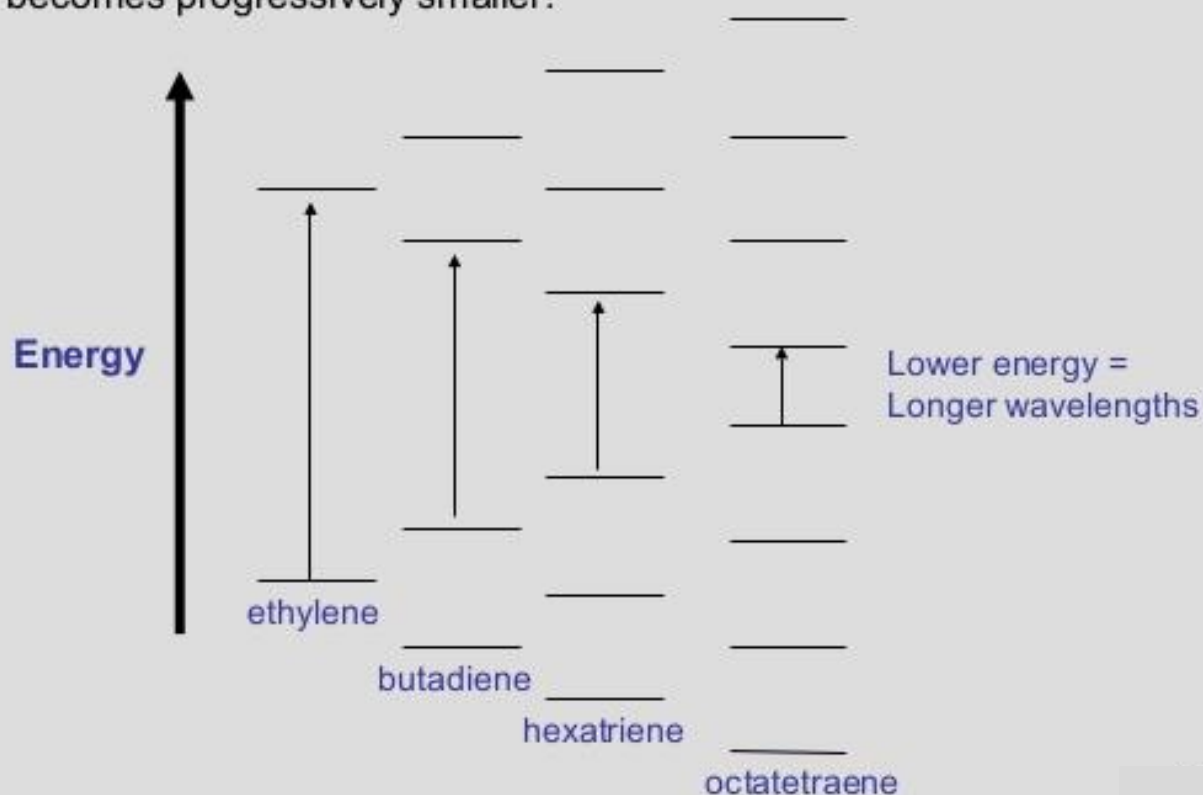
UV Spectroscopy

III. Chromophores

A. Substituent Effects

2. Conjugation – Alkenes

Extending this effect out to longer conjugated systems the energy gap becomes progressively smaller:



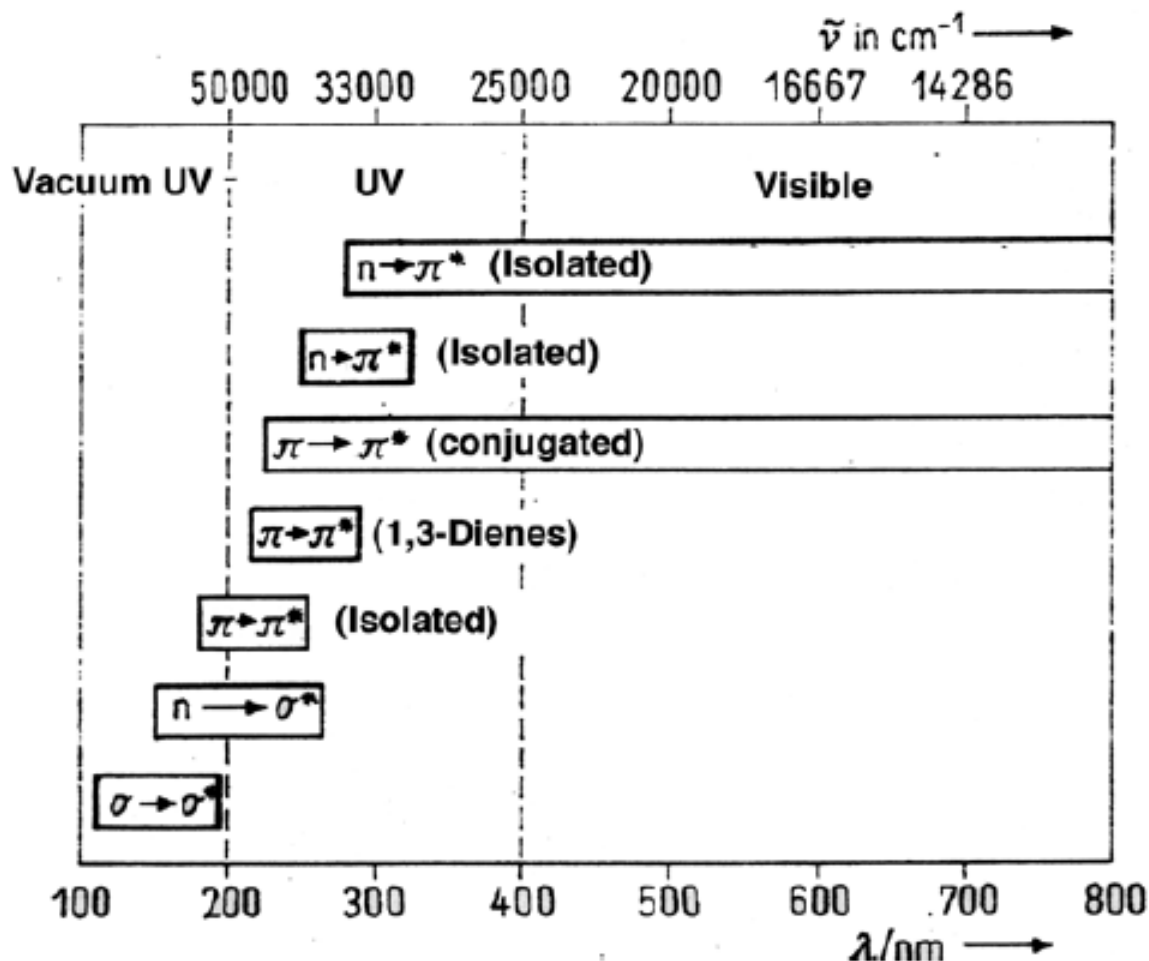
Effect of Conjugation of Chromophores

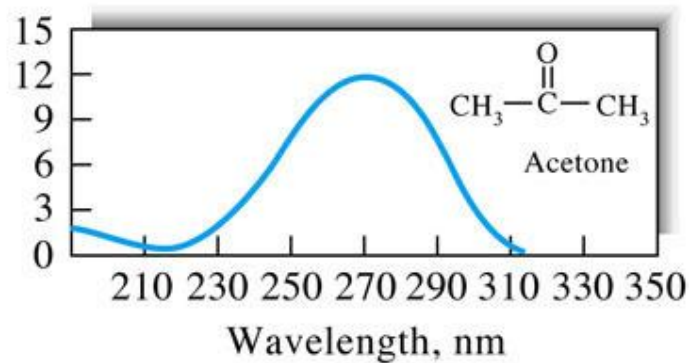
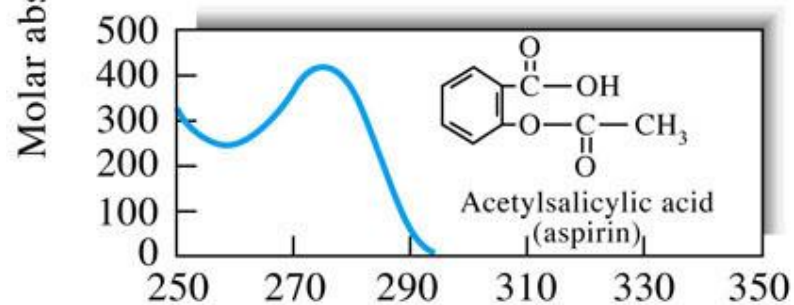
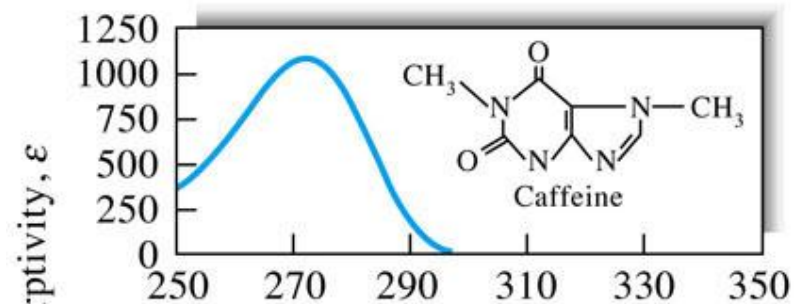
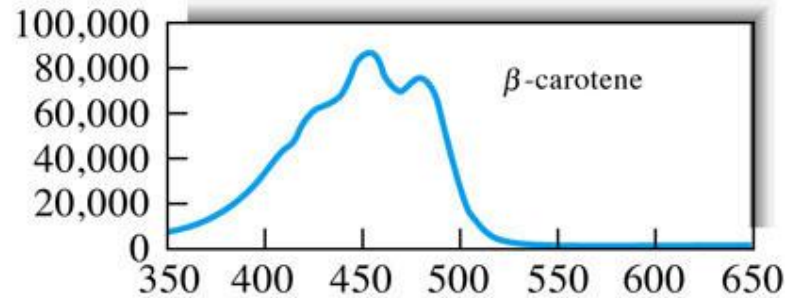
Table 8.3 Values of λ_{max} and ϵ for Ethylene and Conjugated Dienes

Compound	λ_{max} (nm)	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)
$\text{H}_2\text{C}=\text{CH}_2$	165	15,000
	217	21,000
	256	50,000
	290	85,000
	334	125,000
	364	138,000

These transitions correspond to simple bonds and are common to all molecules.

$\pi \rightarrow \pi^*$ transitions depend on the conjugation, so it can reach the visible region of radiation, causing the color of substances.

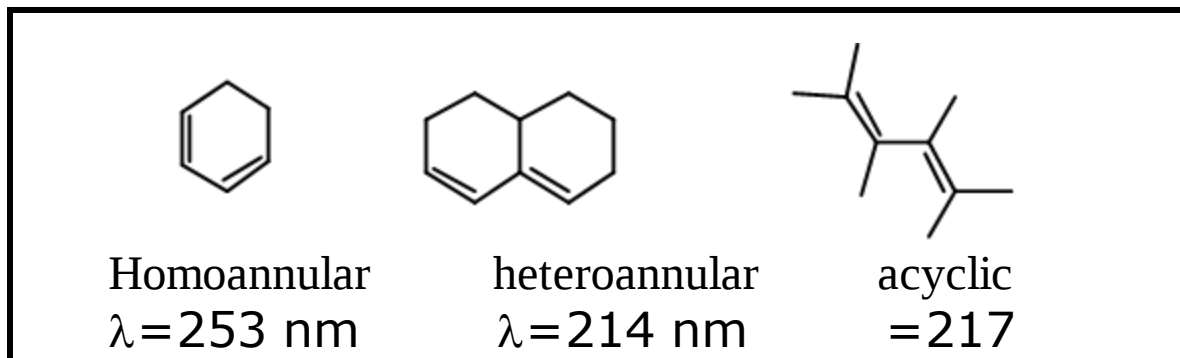




Empirical Rules for Calculating Uv/Vis Absorptions

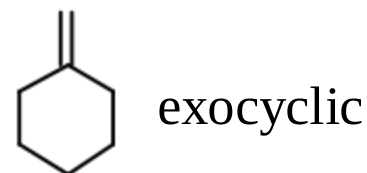
Woodward-Fieser Rules for Calculating the λ_{max} of Conjugated Dienes and Polyenes

- Parent:



- Increments for:

Double bond extending conjugation	+30
Alkyl substituent or ring residue	+5
Exocyclic double bond	+5



Polar groupings:

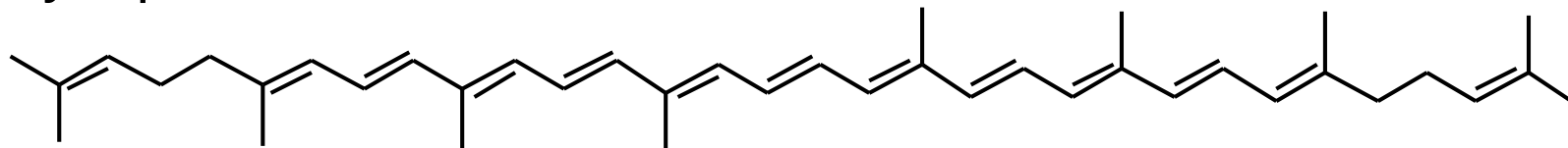
-OC(O)CH ₃	+0
-OR	+6
-Cl, -Br	+5
-NR ₂	+60
-SR	+30

For more than 4 conjugated double bonds:

$$\lambda_{\max} = 114 + 5(\text{number of alkyl groups}) + n(48.0 - 1.7n)$$

Example:

Lycopene:



$$\lambda_{\max} = 114 + 5(8) + 11*(48.0 - 1.7*11) = 476 \text{ nm}$$

$$\lambda_{\max}(\text{Actual}) = 474.$$

Example 1:

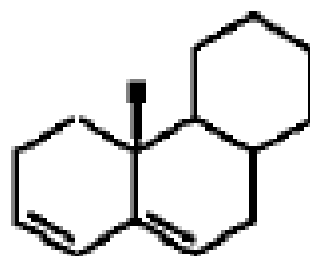


Transoid:		217 nm
Alkyl groups or ring residues:	$3 \times 5 =$	<u>15 nm</u>
Calculated:		232 nm
Observed:		234 nm

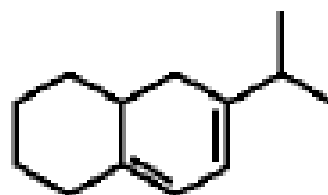
Example 2:



Cisoid:		253 nm
Alkyl groups or ring residues:	$2 \times 5 =$	<u>10 nm</u>
Calculated:		263 nm
Observed:		256 nm



Transoid:		214 nm
Alkyl groups or ring residues:	$3 \times 5 =$	15 nm
Exocyclic double bond:		<u>5 nm</u>
Calculated:		234 nm
Observed:		235 nm



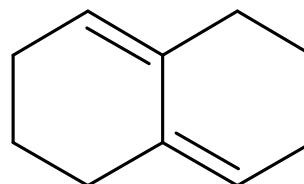
Cisoid:		253 nm
Alkyl groups or ring residues:	4 x 5 =	20 nm
Exocyclic double bond:		<u>5 nm</u>
Calculated:		278 nm
Observed:		275 nm

Example 1

Calculate the λ_{max} for 1,4, dibenzodiene

Solution:

The structure is



Parent heterodiene = 214

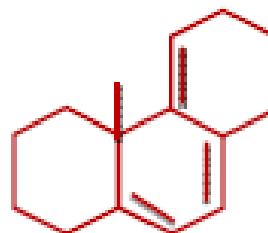
Alkyl substituents (4x5 nm) = 20

Exocyclic double bond 2x5 = 10

$$\lambda_{\text{max}} = 244 \text{ nm (observed 247 nm)}$$

Example 2

Calculate the $\lambda_{\max}$ for



Solution:

The compound is a homoannular diene

Base value = 253

Ring residues (5x5) = 25

Exocyclic double bond 3x5 = 15

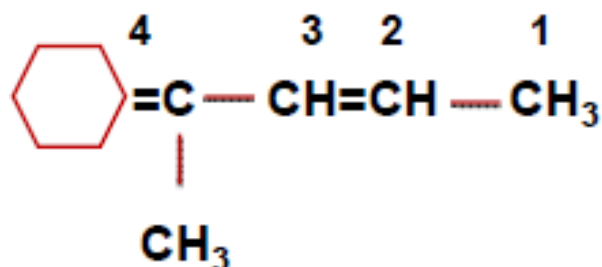
Extended C=C = 30

$\lambda_{\max}$ is 323 nm
observed value is 320 nm.

Example 3

Calculate the absorption maximum for 4 cyclohexenyl
2-pentene

Solution



It is a 2, 4 diene system

Base value	217
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2 Alkyl substituents 2x5	10
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2 Ring residues 2x5	10
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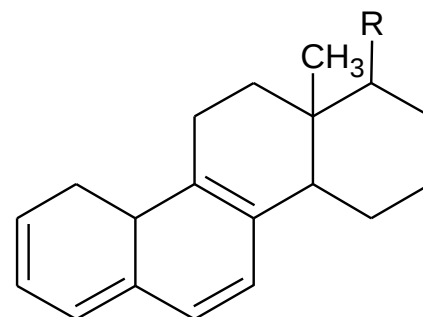
1 Exocyclic bond	5
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242 nm

Observed value is also 242 nm

Example 4

Calculate the $\lambda_{\max}$ for the compound



Solution

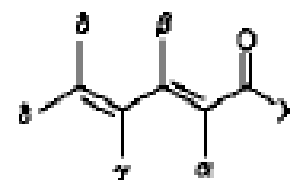
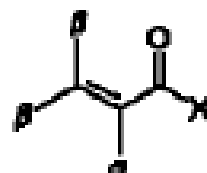
Base value	253 nm
2 Extended double bonds (2x30)	60 nm
5 Ring residues (5x5)	25 nm
1 Exocyclic double bond (1x5)	5 nm

Calculated $\lambda_{\max}$	343 nm
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Observed	345 nm
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Woodward's Rules for Conjugated Carbonyl Compounds

Base values:



X = R

Six-membered ring or acyclic parent enone

$\lambda=215$ nm

Five-membered ring parent enone

$\lambda=202$ nm

X = H

$\lambda=208$ nm

X = OH, OR

$\lambda=195$ nm

Increments for:

Double bond extending conjugation

30

Exocyclic double bond

5

Endocyclic double bond in a 5- or 7-membered ring for X = OH, OR

5

Homocyclic diene component

39

Alkyl substituent or ring residue

α

10

β

12

γ or higher

18

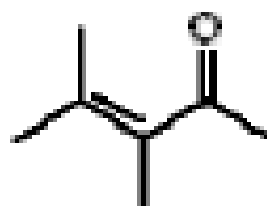
Polar groupings:

-OH	α	35
	β	30
	δ	50
-OC(O)CH ₃	$\alpha, \beta, \gamma, \delta$	6
-OCH ₃	α	35
	β	30
	γ	17
	δ	31
-Cl	α	15
	β, γ, δ	12
-Br	β	30
	α, γ, δ	25
-NR ₂	β	95

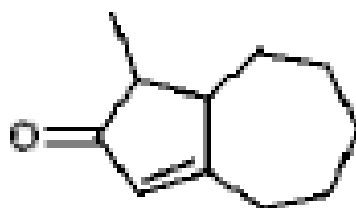
¹Solvent shifts for various solvents:

Solvent	λ_{max} shift (nm)
water	+ 8
chloroform	- 1
ether	- 7
cyclohexane	- 11
dioxane	- 5
hexane	- 11

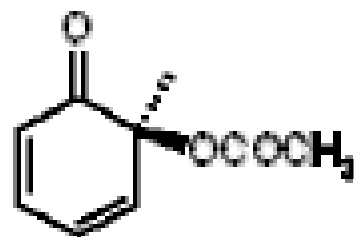
example



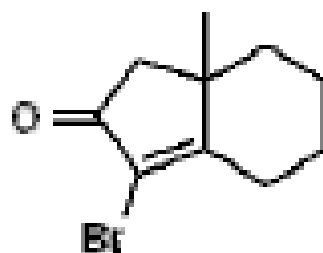
Acyclic enone:		215 nm
α -Alkyl groups or ring residues:		10 nm
β -Alkyl groups or ring residues:	$2 \times 12 =$	<u>24 nm</u>
Calculated:		249 nm
Observed:		249 nm



Five-membered ring parent enone:		202 nm
β -Alkyl groups or ring residues:	$2 \times 12 =$	24 nm
Exocyclic double bond:		<u>5 nm</u>
Calculated:		231 nm
Observed:		226 nm



Six-membered ring or alicyclic parent enone:	215 nm
Extended conjugation:	30 nm
Homocyclic diene component:	39 nm
δ -Alkyl groups or ring residues:	<u>18 nm</u>
Calculated:	302 nm
Observed:	300 nm



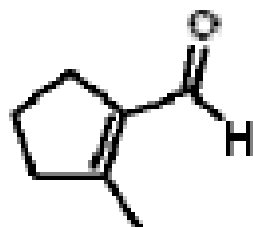
Five-membered ring parent enone:		202 nm
α -Br:		25 nm
β -Alkyl groups or ring residues:	$2 \times 12 =$	24 nm
Exocyclic double bond:		<u>5 nm</u>
Calculated:		256 nm
Observed:		251 nm



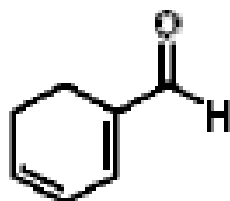
Carboxylic acid:	195 nm
α -Alkyl groups or ring residues:	10 nm
β -Alkyl groups or ring residues:	<u>12 nm</u>
Calculated:	217 nm
Observed:	217 nm



Ester:	195 nm
α -Alkyl groups or ring residues:	10 nm
β -Alkyl groups or ring residues:	12 nm
Endocyclic double bond in 7-membered ring:	<u>5 nm</u>
Calculated:	222 nm
Observed:	222 nm



Aldehyde:		208 nm
α -Alkyl groups or ring residues:		10 nm
β -Alkyl groups or ring residues:	$2 \times 12 =$	<u>24 nm</u>
Calculated:		242 nm
Observed:		242 nm



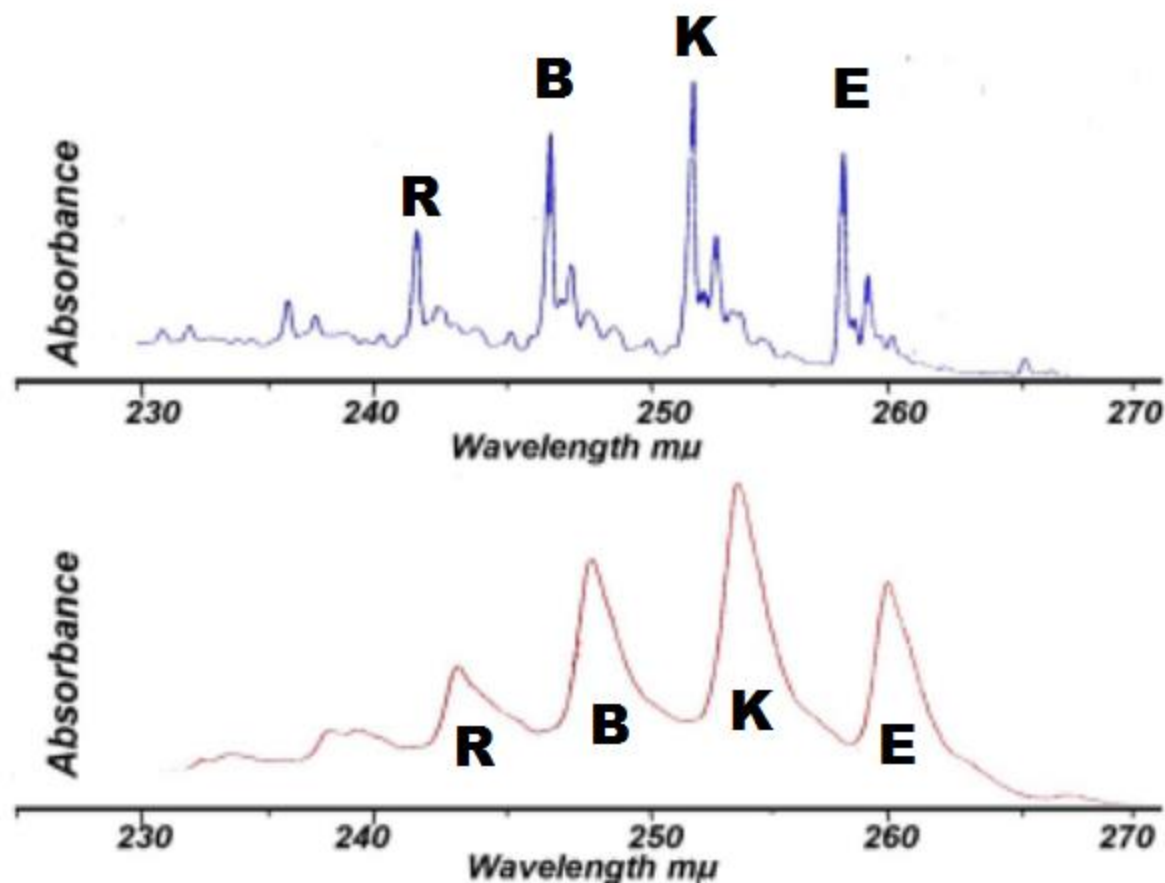
Aldehyde:	208 nm
Extended conjugation:	30 nm
Homodiene component:	39 nm
α -Alkyl groups or ring residues:	10 nm
δ -Alkyl groups or ring residues:	<u>18 nm</u>
Calculated:	304 nm
Observed:	302 nm

Absorption for Mono-Substituted Benzene Derivatives

AROMATIC SYSTEMS

Benzene and many other aromatic compounds shows strong absorption bands at 184 nm (ϵ 47000) and 202 nm (ϵ 7000) and a series of weak bands between 230 – 270 nm. These are associated with vibrational effects on $\pi \rightarrow \pi^*$ transitions. These fine structure bands are susceptible to solvent effects such as alcohols.

ULTRAVIOLET SPECTRUM OF BENZENE

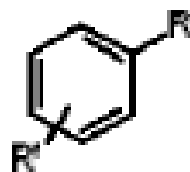




Substituent	E	K	B	R
	($\epsilon > 30000$)	($\epsilon \sim 10000$)	($\epsilon \sim 300$)	($\epsilon \sim 50$)
Electronic Donating Substituents				
none	184	204	254	
-R	189	208	262	
-OH		211	270	
-OR		217	269	
-NH ₂		230	280	
Electronic Withdrawing Substituents				
-F		204	254	
-Cl		210	257	
-Br		210	257	
-I		207	258	
-NH ₃ ⁺		203	254	

π -Conjugating Substituents

$-\text{C}=\text{CH}_2$		248	282	
$-\text{CCH}$	202	248	278	
$-\text{C}_6\text{H}_5$		250		
$-\text{CHO}$		242	280	328
$-\text{C}(\text{O})\text{R}$		238	276	320
$-\text{CO}_2\text{H}$		226	272	
$-\text{CN}$		224	271	
$-\text{NO}_2$		252	280	330



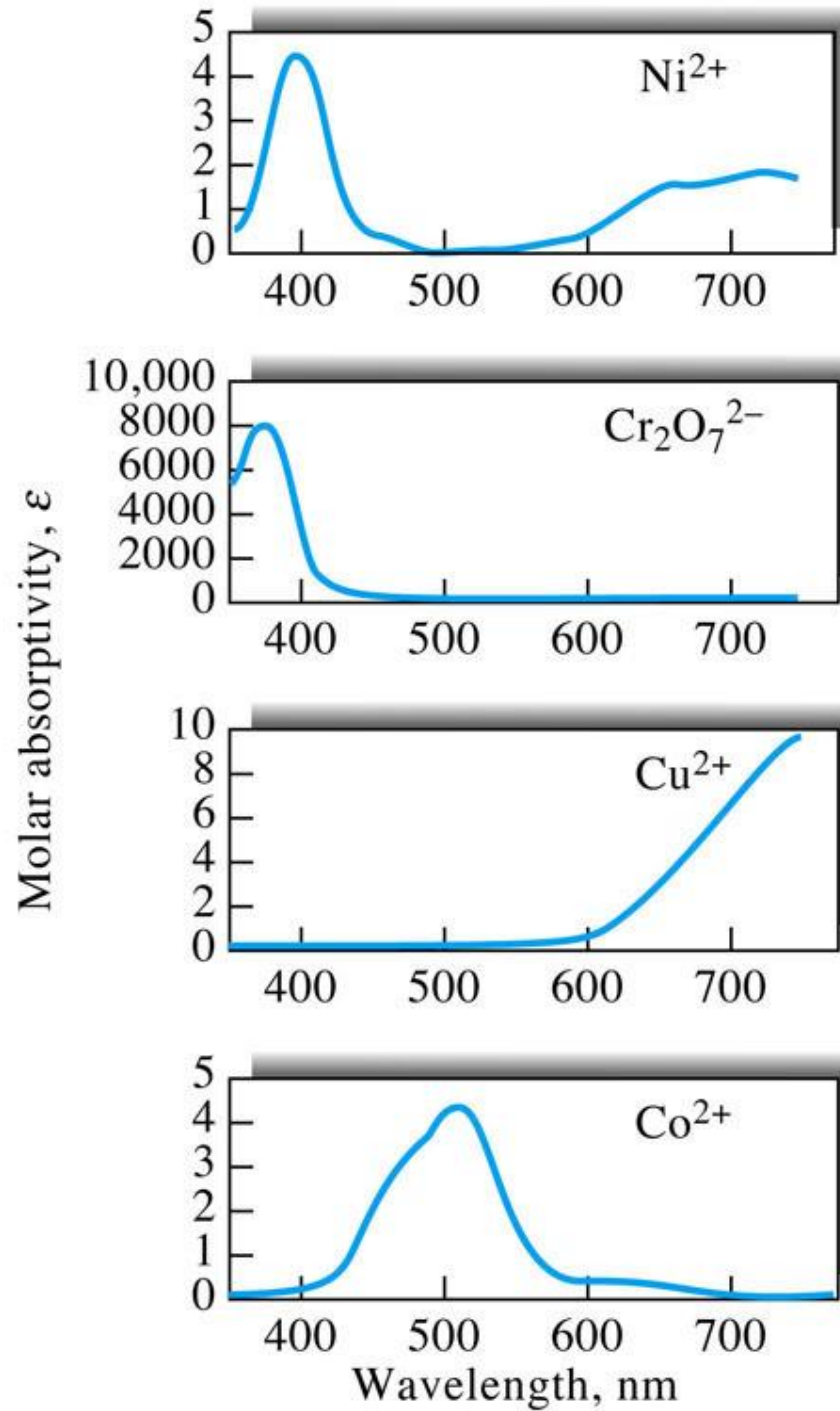
R	R'	Orientation	K		B	
			λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}
-OH	-OH	ortho	214	6000	278	2630
-OR	-CHO	ortho	253	11000	319	4000
-NH ₂	-NO ₂	ortho	229	16000	275	5000
-OH	-OH	meta	277	2200		
-OR	-CHO	meta	252	8300	314	2800
-NH ₂	-NO ₂	meta	235	16000	373	1500
-OH	-OH	para	225	5100	293	2700
-OR	-CHO	para	277	14800		
-NH ₂	-NO ₂	para	229	5000	375	16000
-Ph	-Ph	meta	251	44000		
-Ph	-Ph	para	280	25000		

Benzoyl derivative

Absorption Involving d and f Electrons

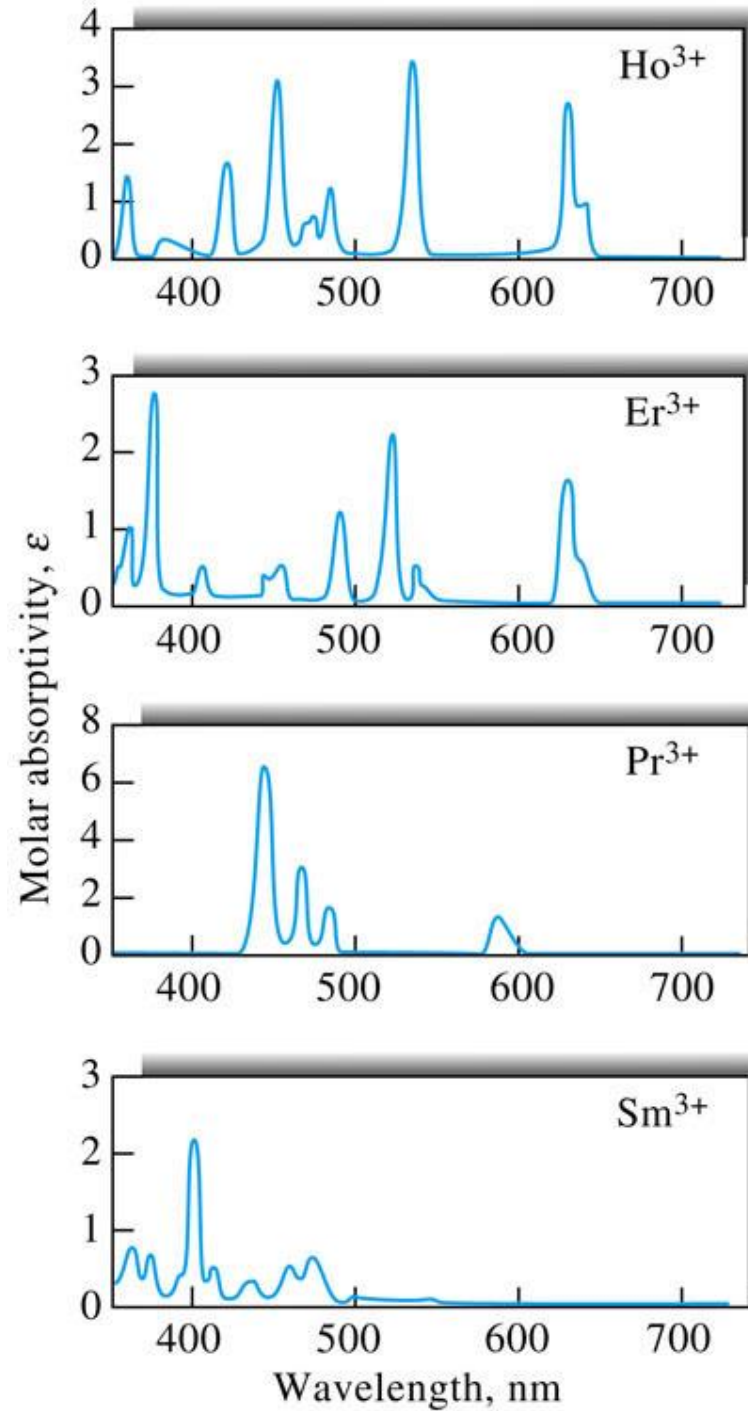
Most transition-metal ions absorb in the ultraviolet or visible region of the spectrum. For the lanthanide and actinide series, the absorption process results from electronic transition of 4f and 5f electrons; for elements of the first and second transition-metal series, the 3d and 4d electrons are responsible.

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
			57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
			89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr
Alkali Metals			Metalloids			Lanthanides											
Alkaline Earth Metals			Nonmetals			Actinides											
Transition Metals			Halogens														
Poor Metals			Noble Gases														



Absorption by Lanthanide and Actinide Ions

The ions of most lanthanide and actinide elements absorb in the ultraviolet and visible regions. Their spectra consist of narrow, well-defined, and characteristic absorption peaks. The transitions responsible for absorption by elements of the lanthanide series appear to involve the various energy levels of 4f electrons, while it is the 5f electrons of the actinide series that interact with radiation.



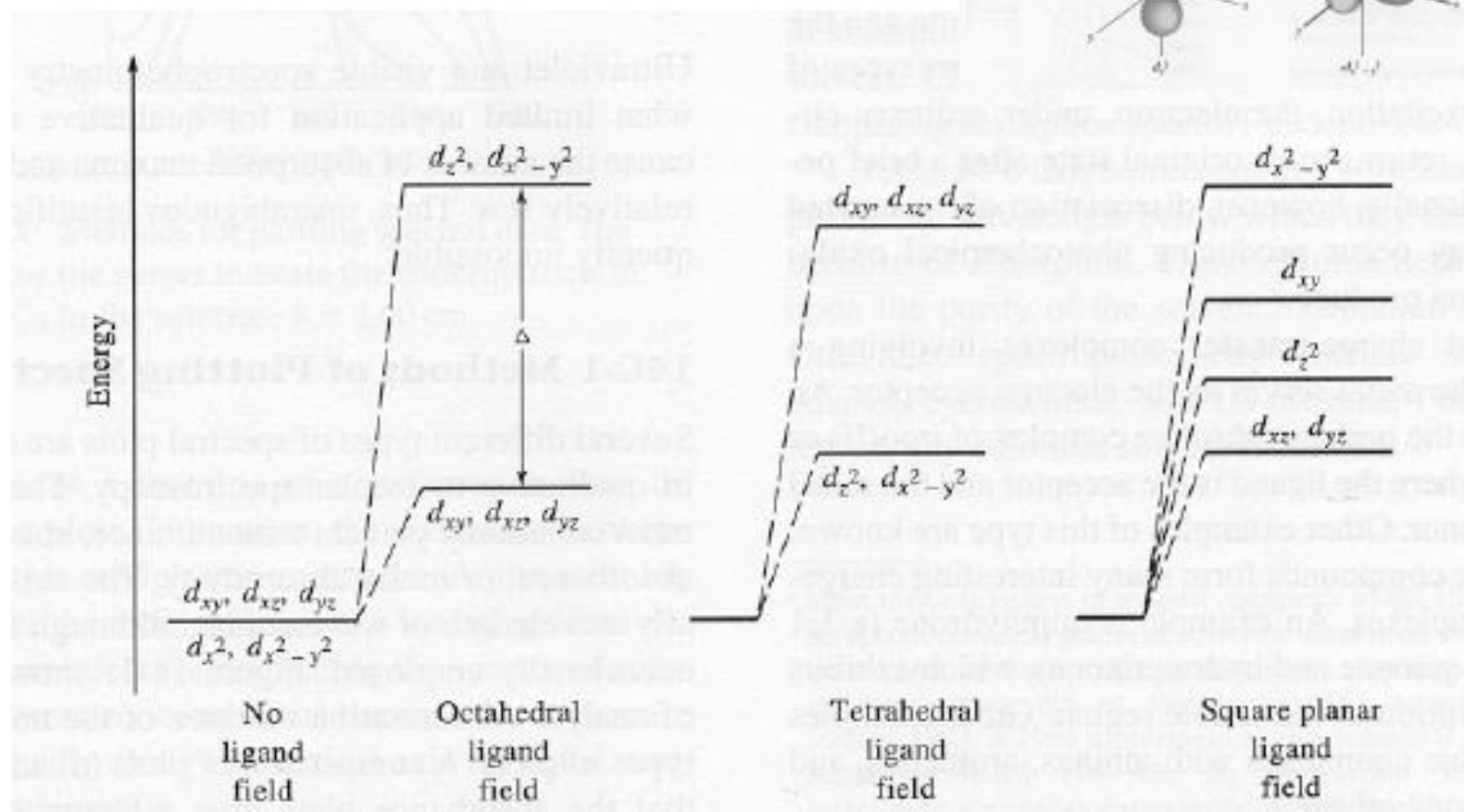
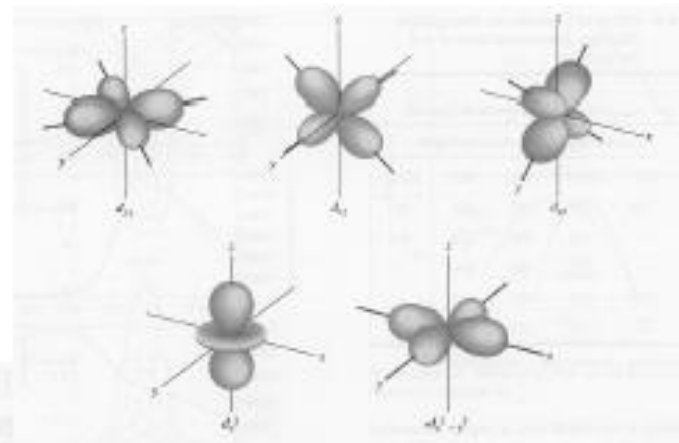
Absorption by Elements of the First and Second Transition-Metal Series

The ions and complexes of the first two transition series tend to absorb visible radiation in one if not all of their oxidation states. The absorption bands are often broad and are strongly influenced by chemical environmental factors. The spectral characteristics of transition metals involve electronic transitions among the various energy levels of d orbitals.

Charge-Transfer Absorption

Species that exhibit charge-transfer absorption are of particular importance because their molar absorptivities are very large ($\epsilon_{\text{max}} > 10,000$). Thus, these complexes provide a highly sensitive means for detecting and determining absorbing species. Complexes exhibit charge transfer absorption are called charge-transfer complexes. In order for a complex to exhibit a charge-transfer spectrum, it is necessary for one of its components to have electron-donor characteristics and for the other component to have electron-acceptor properties. Absorption of radiation then involves transfer of an electron from the donor to an orbital that is largely associated with the acceptor.

Crystal-Field Theory (Ligand-Field Theory): Ligand effect on energy



type of transition	Molar absorptivity ϵ (L/mol·cm)
$\pi-\pi^*$	thousands
$\sigma-\sigma^*$	hundred - thousands
d-d	10-100
charge transfer	>10.000

