

Chemistry 4631

Instrumental Analysis

Lab Lecture 2

More UV Theory

Theory for UV/vis Spectrometry

Molar Absorptivities

Range 0 to 10^5

Magnitude of ϵ depends on capture cross section of the species and probability of the energy-absorbing transition.

$$\epsilon = 8.7 \times 10^{19} P A$$

P – transition probability

A – cross-section target area, cm^2

Theory for UV/vis Spectrometry

Molar Absorptivities

$$\epsilon = 8.7 \times 10^{19} P A$$

P – transition probability

A – cross-section target area, cm^2

Typical area for organic molecules are $\sim 10^{-15} \text{ cm}^2$

P – range from 0 to 1

quantum allowed 0.1 to 1 ($\epsilon_{\text{max}} = 10^4$ to 10^5)

Less than 10^3 – gives low intensity

Theory for UV/vis Spectrometry

Absorbing Species

Absorption of UV/vis radiation is a two step process:



M^* lifetime $\sim 10^{-8}$ to 10^{-9} sec



Theory for UV/vis Spectrometry

Absorbing Species

Relaxation occurs by:

- Conversion to heat
- Decomposition of M^* (photochemical rxn)
- Reemission of fluorescence or phosphorescence

Theory for UV/vis Spectrometry

Absorbing Species

Absorption occurs by excitation of bonding electrons

i.e. λ correlates to type of bond in species

Valuable in identifying functional groups

Theory for UV/vis Spectrometry

Absorbing Species

Three types of electronic transitions:

- π , σ , and n electrons
- d and f electrons
- charge transfer electrons

Theory for UV/vis Spectrometry

Absorbing Species that contain π , σ , and n electrons are:

- Organic molecules
- Organic ions
- Many inorganic anions

Absorption of UV above the vacuum UV region is limited to functional groups (chromophores) that contain valence electrons at low excitation energies.

Theory for UV/vis Spectrometry

Types of Absorbing Electrons

Electrons of organic molecules contributing to absorption are:

- **Those in bond formation between atoms**
- **Nonbonding or unshared outer electrons that are localized (i.e. oxygen, halogens, sulfur, nitrogen)**

Theory for UV/vis Spectrometry

Two atomic orbitals combine to produce:

- Low energy bonding molecular orbital
- High energy antibonding molecular orbital

Single bonds – sigma (σ) orbitals

Double bonds – sigma (σ) and pi (π) orbitals

Nonbonding electrons - n

Theory for UV/vis Spectrometry

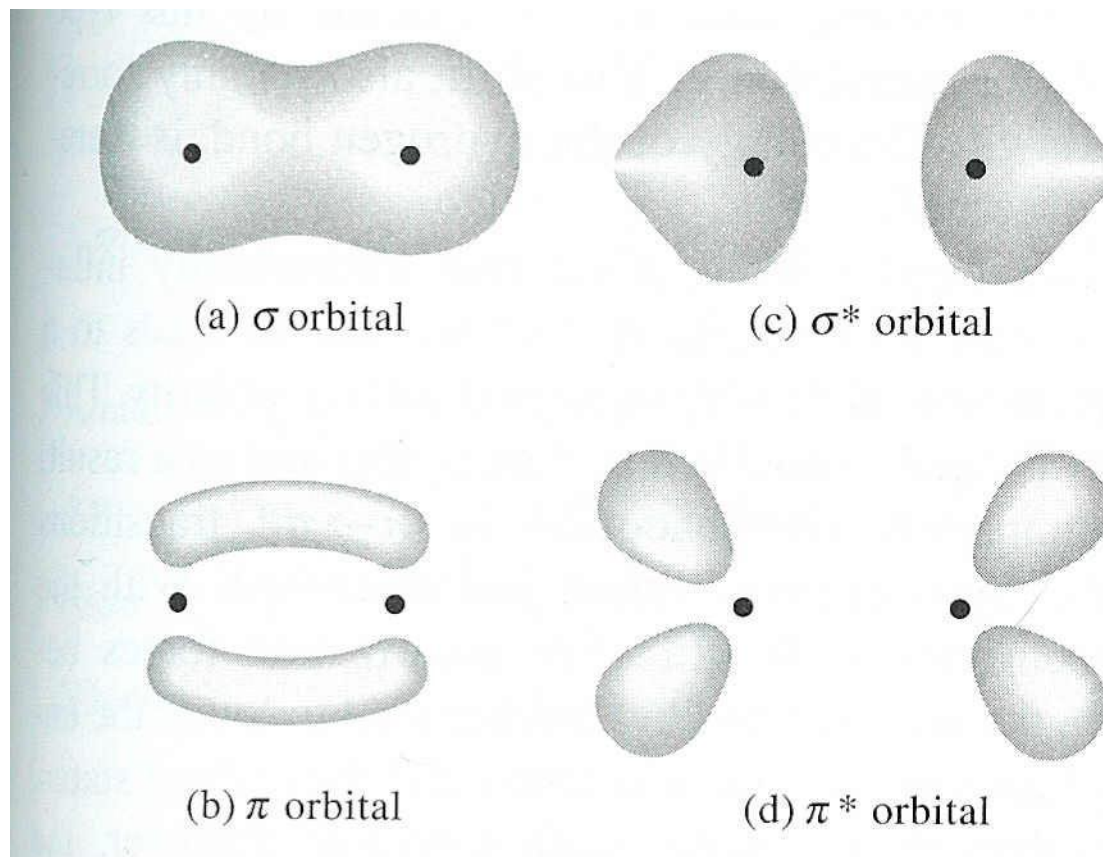


Figure 14-1 Electron distribution in sigma and pi molecular orbitals.

Theory for UV/vis Spectrometry

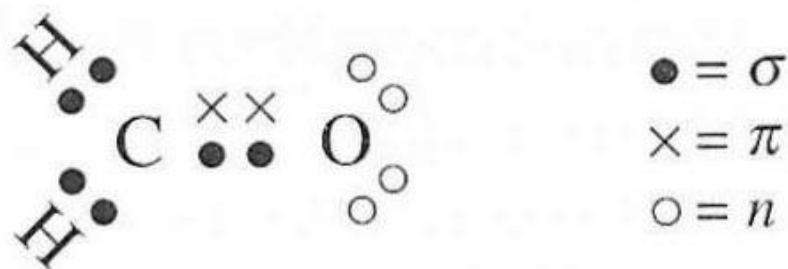


Figure 14-2 Types of molecular orbitals in formaldehyde.

Theory for UV/vis Spectrometry

Electronic transitions are designated as

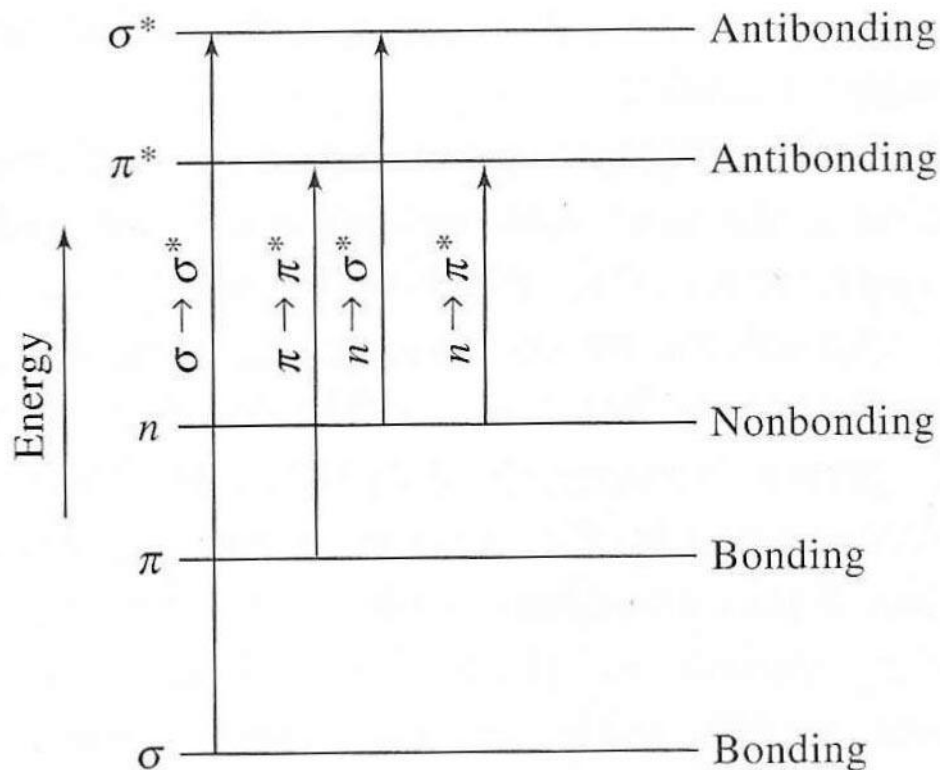


Figure 14-3 Electronic molecular energy levels.

Theory for UV/vis Spectrometry

$\sigma \rightarrow \sigma^*$ Transitions

Energy to promote a transition is large needing far UV.

Examples:

C-H bonds in methane seen at 125 nm.

C-C bonds in ethane at 135 nm.

Theory for UV/vis Spectrometry

$n \rightarrow \sigma^*$ Transitions

Occur in compounds containing atoms with unshared electrons.

Absorption region 150 to 250 nm

Theory for UV/vis Spectrometry

TABLE 14-1 Some Examples of Absorption due to $n \rightarrow \sigma^*$ Transitions^a

Compound	λ_{\max} (nm)	ϵ_{\max}
H ₂ O	167	1480
CH ₃ OH	184	150
CH ₃ Cl	173	200
CH ₃ I	258	365
(CH ₃) ₂ S ^b	229	140
(CH ₃) ₂ O	184	2520
CH ₃ NH ₂	215	600
(CH ₃) ₃ N	227	900

^aSamples in vapor state.

^bIn ethanol solvent.

Theory for UV/vis Spectrometry

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

Absorption region 200 – 700 nm

Transition requires presence of unsaturated functional groups to provide π orbitals.

TABLE 14-1 Absorption Characteristics of Some Common Chromophores

Chromophore	Example	Solvent	λ_{\max} , nm	ϵ_{\max}	Transition Type
Alkene	$C_6H_{13}CH=CH_2$	<i>n</i> -Heptane	177	13,000	$\pi \rightarrow \pi^*$
Alkyne	$C_5H_{11}C\equiv C-CH_3$	<i>n</i> -Heptane	178	10,000	$\pi \rightarrow \pi^*$
			196	2000	—
			225	160	—
Carbonyl	$\begin{array}{c} CH_3CCH_3 \\ \\ O \end{array}$	<i>n</i> -Hexane	186	1000	$n \rightarrow \sigma^*$
			280	16	$n \rightarrow \pi^*$
Carboxyl	$\begin{array}{c} CH_3CH \\ \\ O \end{array}$	<i>n</i> -Hexane	180	large	$n \rightarrow \sigma^*$
			293	12	$n \rightarrow \pi^*$
Amido	$\begin{array}{c} CH_3COOH \\ \\ O \end{array}$	Ethanol	204	41	$n \rightarrow \pi^*$
	$\begin{array}{c} CH_3CNH_2 \\ \\ O \end{array}$	Water	214	60	$n \rightarrow \pi^*$
Azo	$CH_3N=NCH_3$	Ethanol	339	5	$n \rightarrow \pi^*$
Nitro	CH_3NO_2	Isooctane	280	22	$n \rightarrow \pi^*$
Nitroso	C_4H_9NO	Ethyl ether	300	100	—
			665	20	$n \rightarrow \pi^*$
Nitrate	$C_2H_5ONO_2$	Dioxane	270	12	$n \rightarrow \pi^*$

Theory for UV/vis Spectrometry

Solvent Effects

Increasing polarity of the solvent:

- Shifts $n \rightarrow \pi^*$ transitions to shorter λ 's (blue shift).
- Shifts $\pi \rightarrow \pi^*$ Transitions to higher λ 's (red shift).

Blue shift – from increase solvation of the unbonded electron pair, lowering the energy of the n orbital.

Example: water or alcohol as solvents increases hydrogen bond formation.

Theory for UV/vis Spectrometry

TABLE 14-3 Effect of Multichromophores on Absorption

Compound	Type	λ_{\max} (nm)	ϵ_{\max}
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	Olefin	184	~10,000
$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}=\text{CH}_2$	Diolefin (unconjugated)	185	~20,000
$\text{H}_2\text{C}=\text{CHCH}=\text{CH}_2$	Diolefin (conjugated)	217	21,000
$\text{H}_2\text{C}=\text{CHCH}=\text{CHCH}=\text{CH}_2$	Triolefin (conjugated)	250	—
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CCH}_3 \end{array}$	Ketone	282	27
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CCH}_3 \end{array}$	Unsaturated ketone (unconjugated)	278	30
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2=\text{CHCCH}_3 \end{array}$	α,β -Unsaturated ketone (conjugated)	324	24
		219	3,600

Theory for UV/vis Spectrometry

Absorbing Species

Three types of electronic transitions:

- π , σ , and n electrons
- d and f electrons**
- charge transfer electrons

Theory for UV/vis Spectrometry

Absorption involving d and f electrons

Many transitions-metal ions absorb in UV or vis region.

The lanthanide and actinide series give narrow well-defined peaks and are not affected by environment (shielding of f electrons).

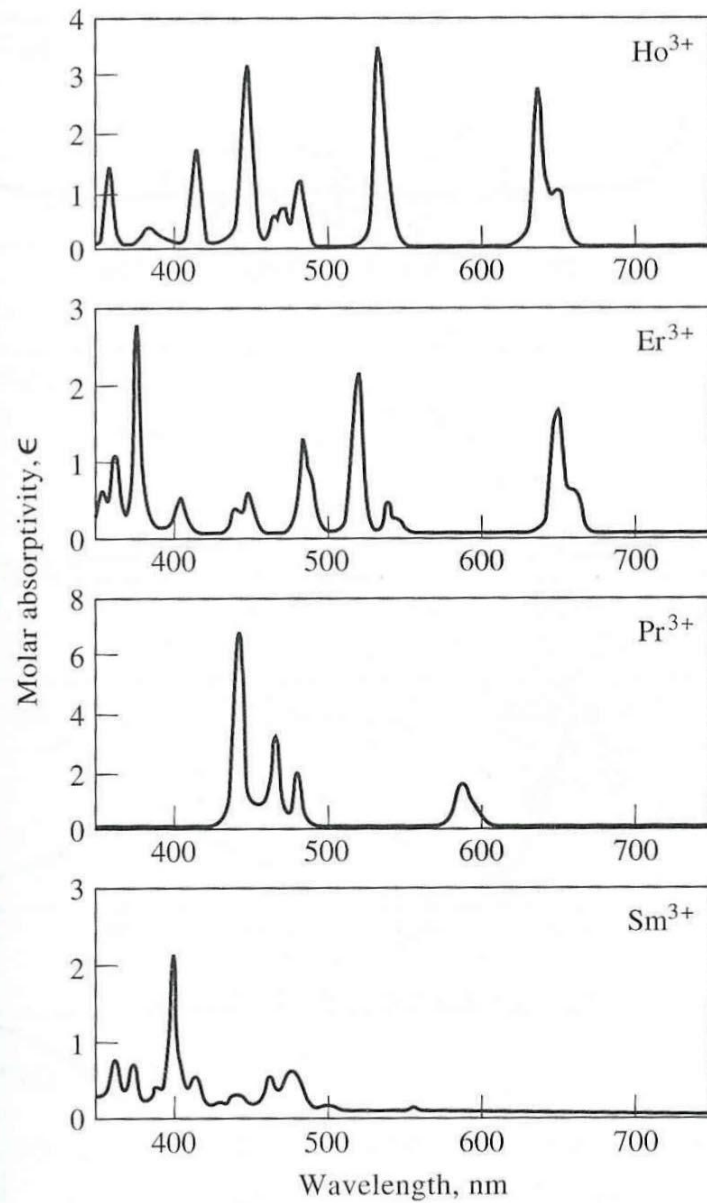


Figure 14-6 Typical absorption spectra for lanthanide ions.

Theory for UV/vis Spectrometry

Absorption involving d and f electrons

The transition metal ion and complexes give broad bands and are influenced by environment.

Theory for UV/vis Spectrometry

Absorption involving d and f electrons

Two theories are proposed to explain the intense influence of environment on transition-metal ions.

- Crystal field theory
- Molecular orbital theory

Theory for UV/vis Spectrometry

Absorption involving d and f electrons

Complex formation between the metal ion and a ligand causes splitting of the d-orbital energies.

The approach of the ligand along an axis containing a d-orbital will have a repulsive effect and increase the energy of the d-orbital.

Theory for UV/vis Spectrometry

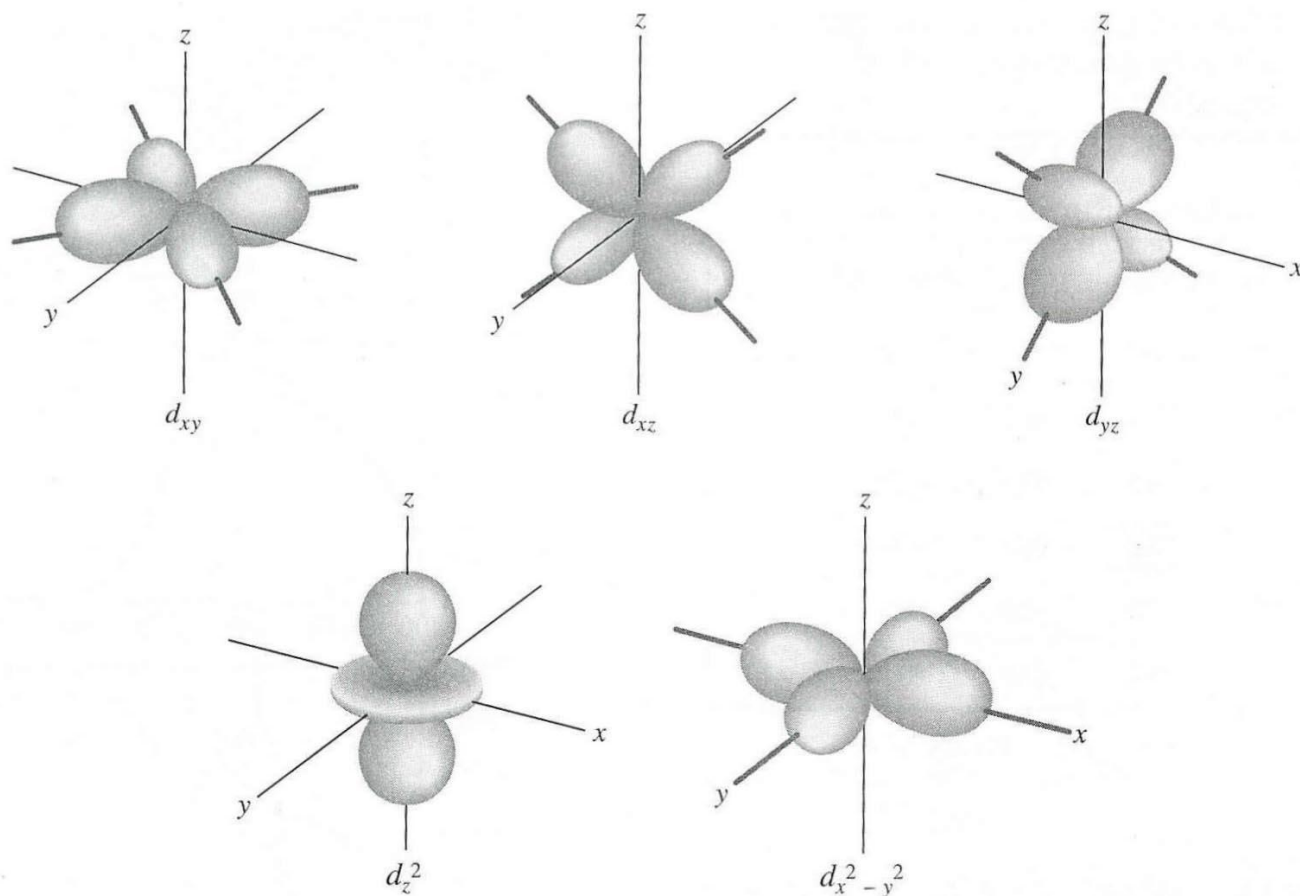


Figure 14-8 Electron-density distribution in the five d orbitals.

Theory for UV/vis Spectrometry

Crystal field theory (Ligand field theory)

The five d orbitals are degenerate (equal energy) in gaseous metal ions.

However in an electrostatic field caused by the presence of ligands this is no longer true.

Theory for UV/vis Spectrometry

Crystal field theory

Example :

Octahedral complex with d_{z^2} and $d_{x^2-y^2}$ directed towards the ligands.

Ligand cause repulsion in these two orbitals and raise the energy (e_g^*) more than for the other three orbitals, d_{xy} , d_{xz} , d_{yz} (t_{2g}).

Theory for UV/vis Spectrometry

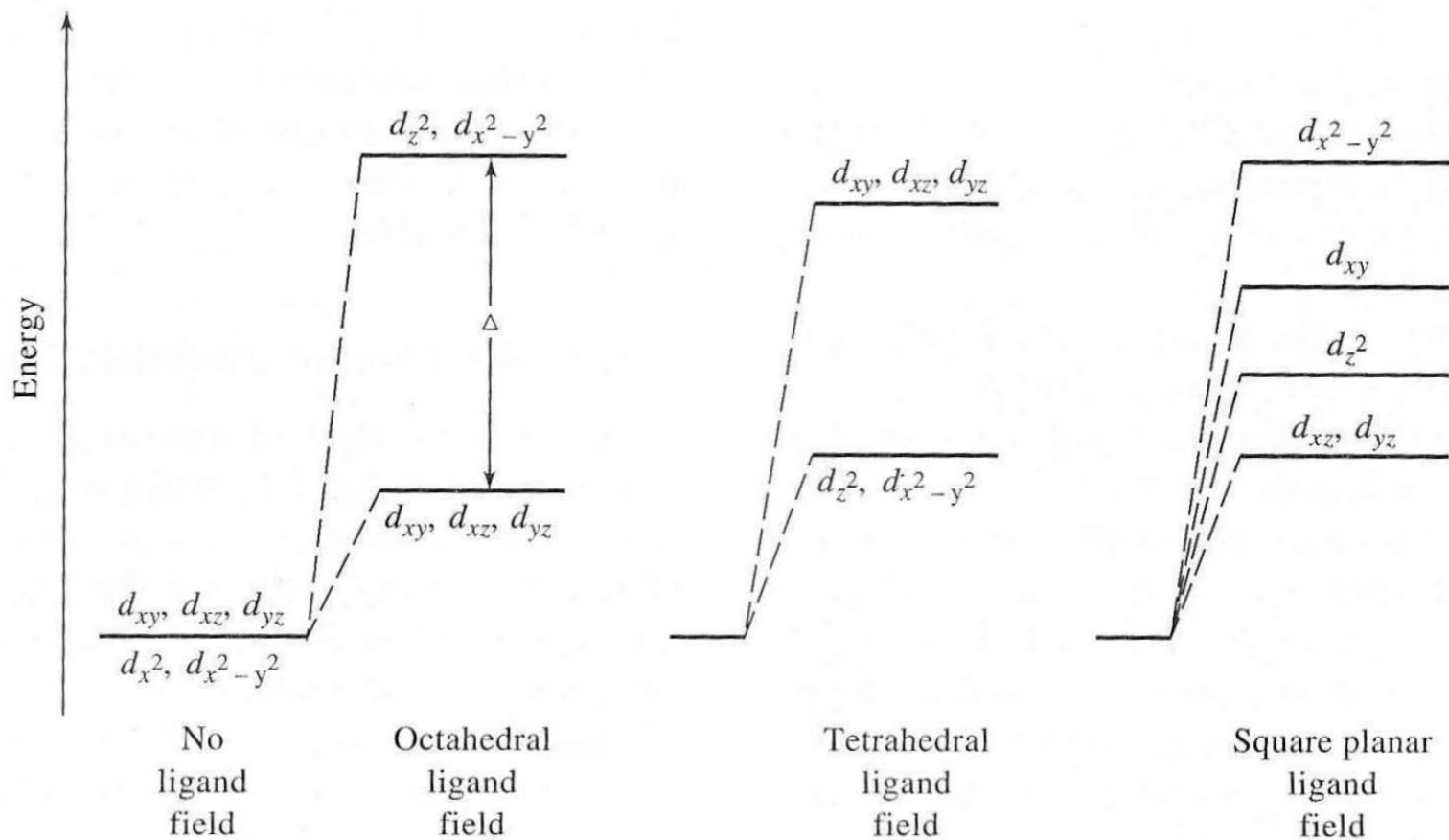


Figure 14-9 Effect of ligand field on d -orbital energies.

Theory for UV/vis Spectrometry

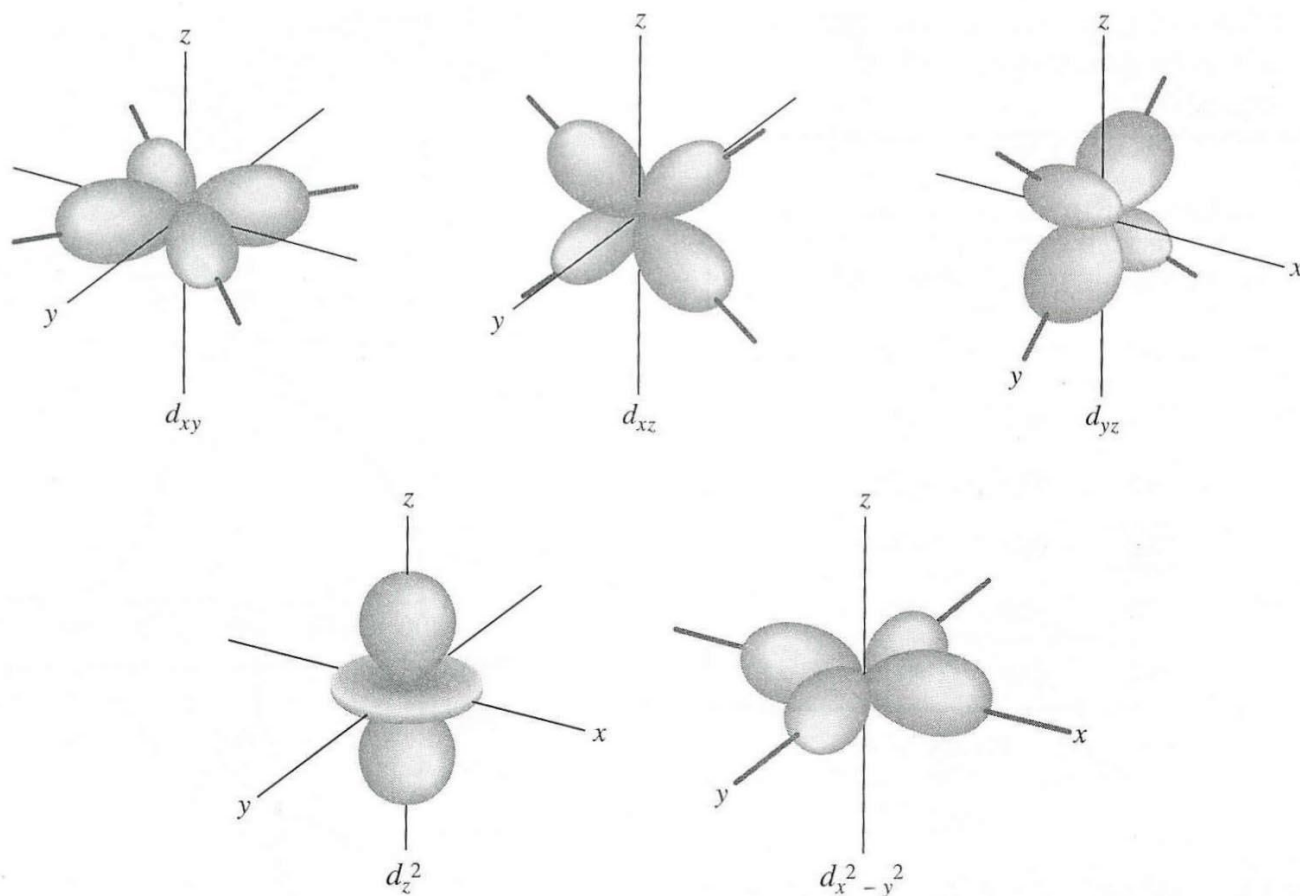


Figure 14-8 Electron-density distribution in the five d orbitals.

Theory for UV/vis Spectrometry

Crystal field theory

The stronger the field, the greater the splitting of the energy levels.

For all configurations other than d^0 , d^5 (high spin) and d^{10} , splitting lowers the total energy of the system.

This decrease in energy caused by the splitting of the energy levels is the ligand field stabilization energy (LFSE).

Theory for UV/vis Spectrometry

Crystal field theory

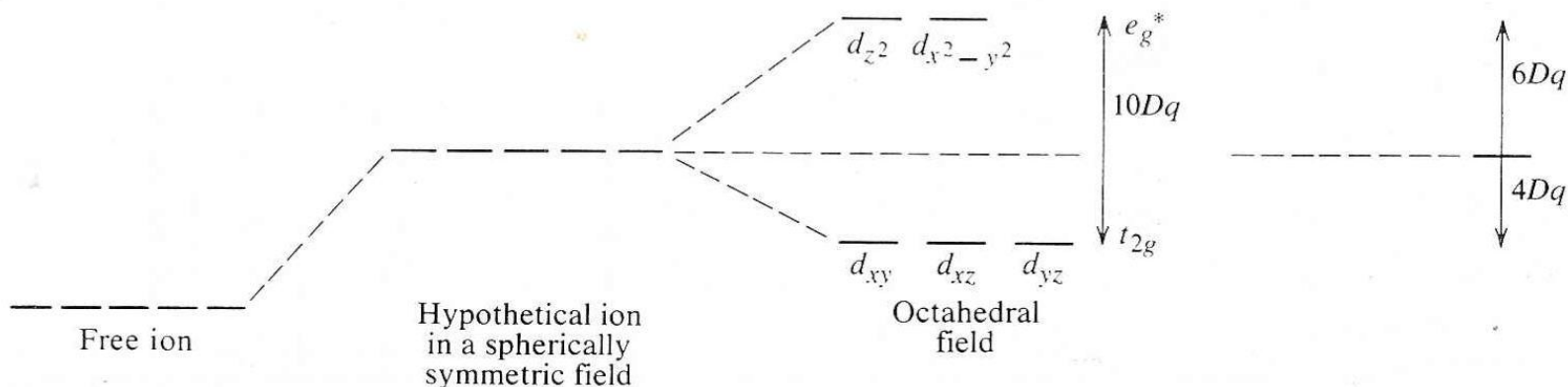


Figure 7.8 Splitting of the d energy levels in an octahedral complex.

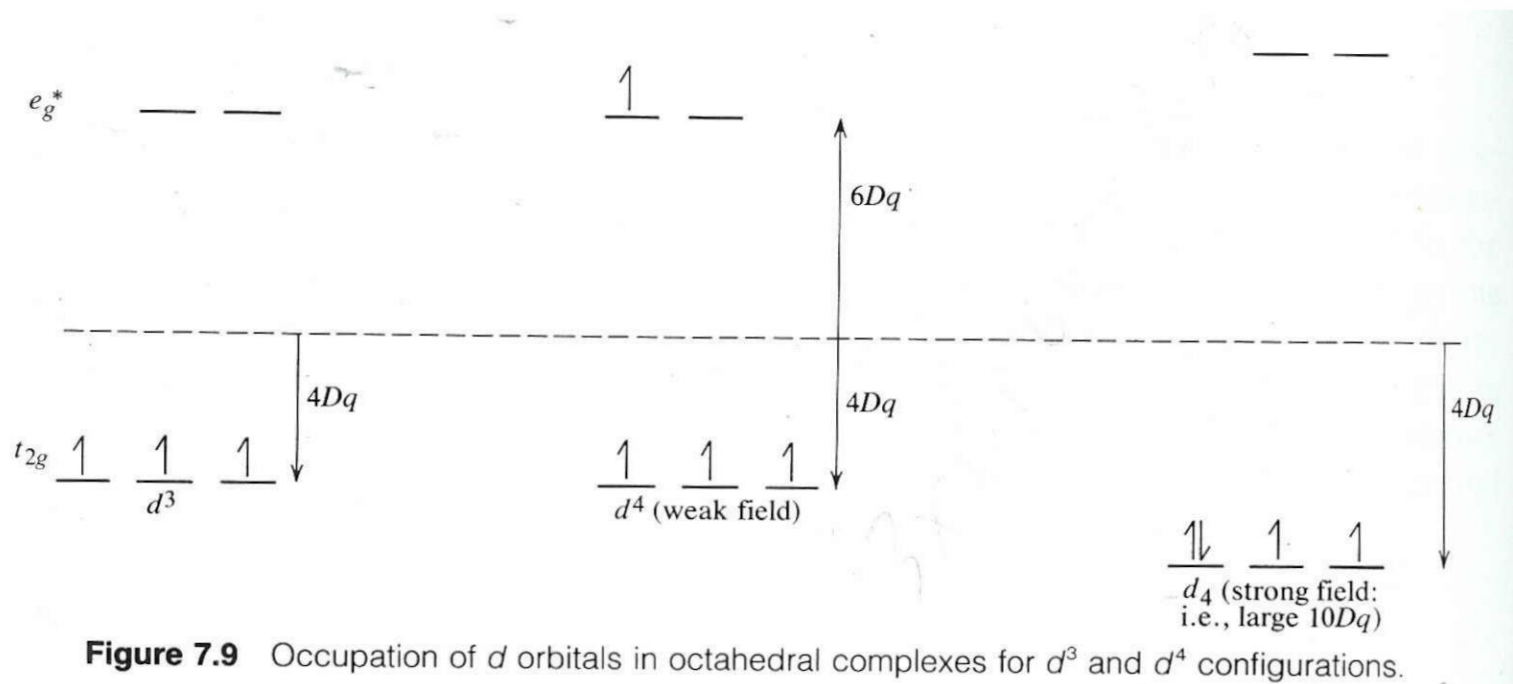
Theory for UV/vis Spectrometry

Crystal field theory

Electrons enter the t_{2g} orbitals in accordance with Hund's rule.

Theory for UV/vis Spectrometry

Crystal field theory



Theory for UV/vis Spectrometry

Crystal field theory

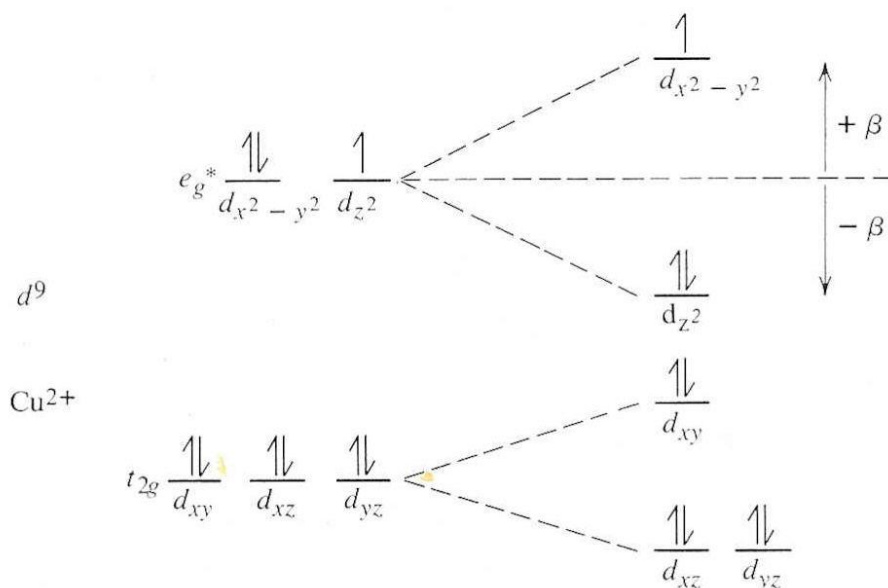


Figure 7.10 Splitting of the energy levels in an octahedral (tetragonal) field elongated along the z direction.

Theory for UV/vis Spectrometry

Crystal field theory

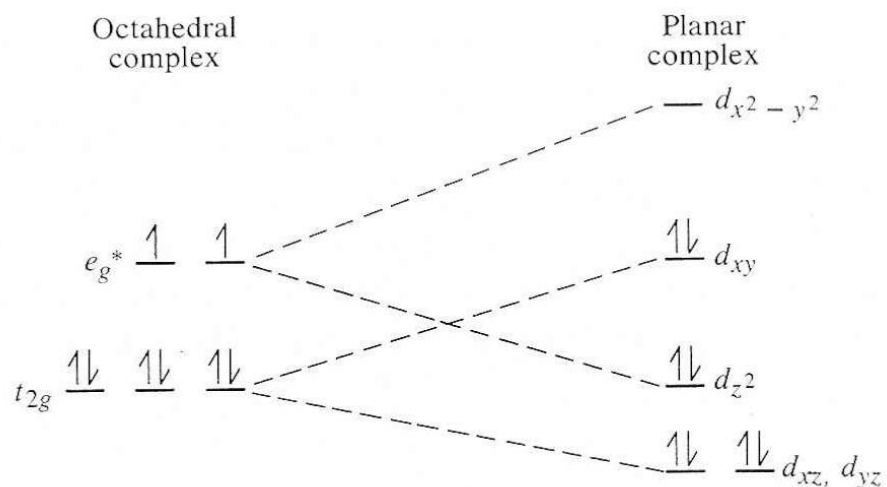


Figure 7.11 Energy levels for square planar nickel(II) complexes.

Theory for UV/vis Spectrometry

Absorption involving d and f electrons

The magnitude of the energy splitting depends on:

- Charge on the metal ion (increases with increasing oxidation number)
- Position of the parent element in the periodic table (increases down a group)
- Ligand field strength

Theory for UV/vis Spectrometry

Ligand field strength

$I^- < Br^- < Cl^- < F^- < OH^- < C_2O_4^{2-} \sim H_2O < SCN^- < NH_3 < \text{ethylenediamine} < o\text{-phenanthroline} < NO_2^- < CN^-$

Theory for UV/vis Spectrometry

Ligand field strength

$I^- < Br^- < Cl^- < F^- < OH^- < C_2O_4^{2-} \sim H_2O < SCN^- < NH_3 < \text{ethylenediamine} < \text{o-phenanthroline} < NO_2^- < CN^-$

This is also known as the spectrochemical series, since the original order was determined from spectral shifts for complexes.

Theory for UV/vis Spectrometry

TABLE 14-5 Effect of Ligands on Absorption Maxima Associated with $d \rightarrow d$ Transitions

Central Ion	$\lambda_{\max}(\text{nm})$ for the Indicated Ligands				
	Increasing Ligand Field Strength \rightarrow				
	6Cl^-	$6\text{H}_2\text{O}$	6NH_3	3en^a	6CN^-
Cr(III)	736	573	462	456	380
Co(III)	—	538	435	428	294
Co(II)	—	1345	980	909	—
Ni(II)	1370	1279	925	863	—
Cu(II)	—	794	663	610	—

^aen = ethylenediamine, a bidentate ligand = $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

Theory for UV/vis Spectrometry

Absorbing Species

Three types of electronic transitions:

- π , σ , and n electrons
- d and f electrons
- charge transfer electrons

Theory for UV/vis Spectrometry

Charge Transfer Absorption

Molar absorptivities for charge transfer complexes are very large ($\epsilon_{\text{max}} > 10,000$)

Examples are inorganic complexes such as some complexes of Fe (II) and Fe (III).

Theory for UV/vis Spectrometry

Charge Transfer Absorption

For a complex to exhibit charge transfer absorption, one of its components is an electron-donor and another is an electron-acceptor.

Absorption then is a transfer of an electron from the donor to the acceptor.

Theory for UV/vis Spectrometry

Charge Transfer Absorption

Ex: For a Fe(III)/thiocyanate complex, when a photon is absorbed, an electron is transferred from the thiocyanate ion to the Fe(III) producing Fe(II).

Applications of UV/vis Spectrometry

Derivative Spectroscopy

Spectra are 1st or 2nd order derivative of absorbance or transmittance with respect to wavelength.

Advantages

- reveal detail that can be lost in an ordinary spectrum
- help identify overlapping peaks
- reveal weaker signals

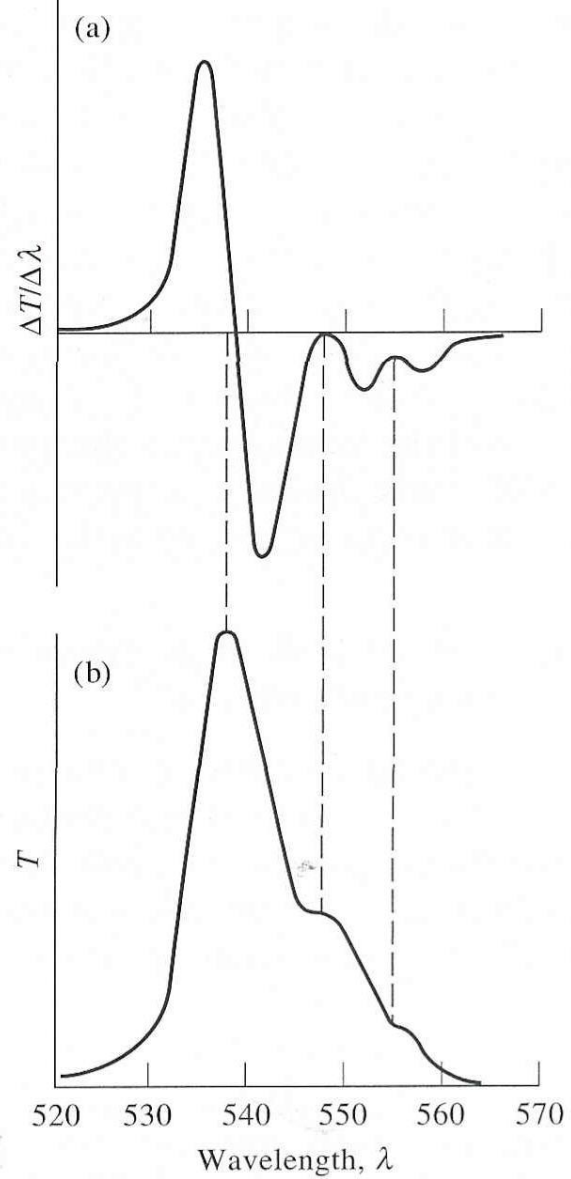


Figure 14-16 Comparison of a derivative spectrum (a) with a standard transmittance spectrum (b).

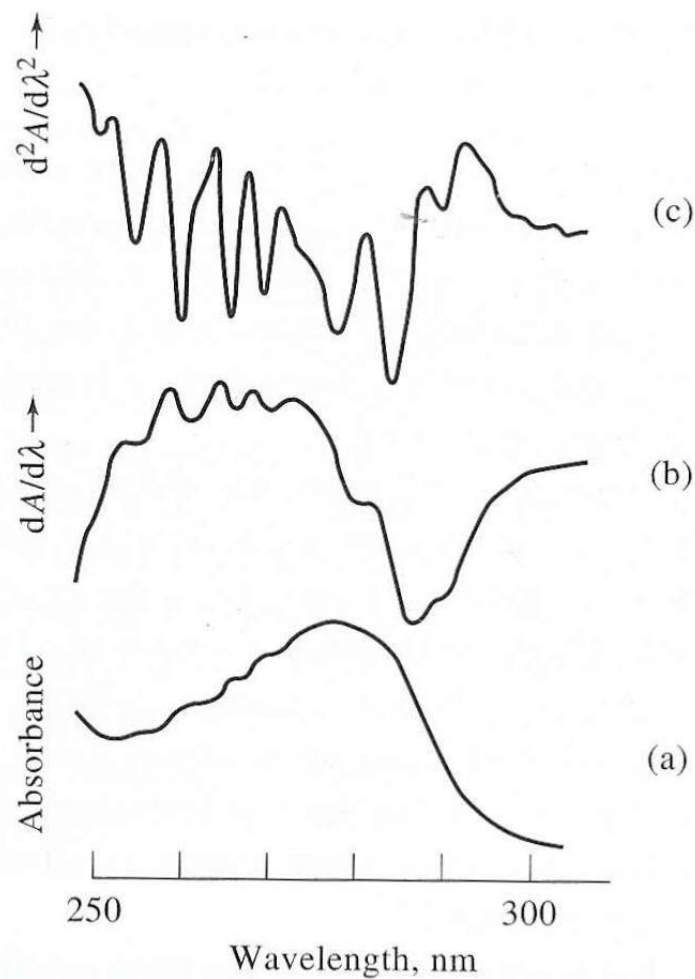


Figure 14-17 Absorption spectra of bovine albumin: (a) ordinary spectrum, (b) first derivative spectrum, (c) second derivative spectrum. (Reprinted with permission from J. E. Cahill and F. G. Padera, *Amer. Lab.*, **1980**, 12(4), 109. Copyright 1980 by International Scientific Communications, Inc.).

Assignment

Read Chapters 6, 7, and 13 from Textbook

