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.

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

P – transition probability

A – cross-section target area, cm^2

Theory for UV/vis Spectrometry

Molar Absorptivities

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

P – transition probability

A – cross-section target area, cm^2

Typical area for organic molecules are ~ 10^{-15} cm^2

P – range from 0 to 1

quantum allowed 0.1 to 1 ($\varepsilon_{max} = 10^4$ 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:

$M + hv \rightarrow M^*$ (electronic excitation)

M^* lifetime ~ 10^{-8} to 10^{-9} sec

$M^* \rightarrow M$ + heat (relaxation)

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:

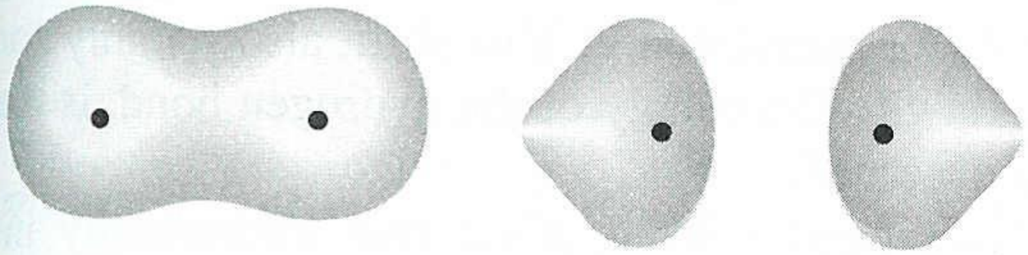
- Low energy bonding molecular orbital
- High energy antibonding molecular orbital

Single bonds – sigma (σ) orbitals

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

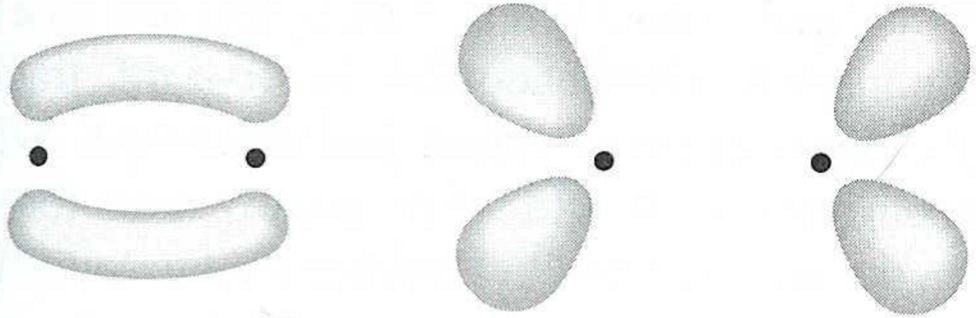
Nonbonding electrons - n

Theory for UV/vis Spectrometry



(a) σ orbital

(c) σ* orbital



(b) π orbital

(d) π * orbital

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

Theory for UV/vis Spectrometry

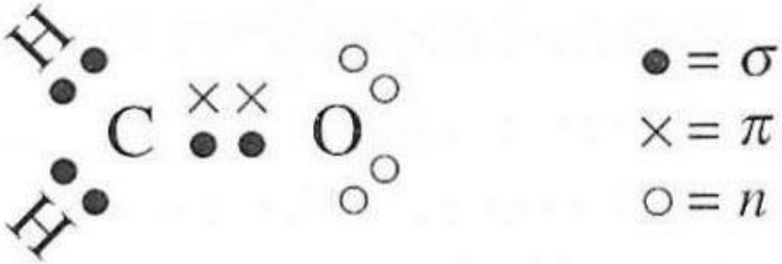


Figure 14-2 Types of molecular orbitals in formaldehyde.

Theory for UV/vis Spectrometry

Electronic transitions are designated as

- **σ → σ***
- **n → σ***
- **n → π***
- **π → π***

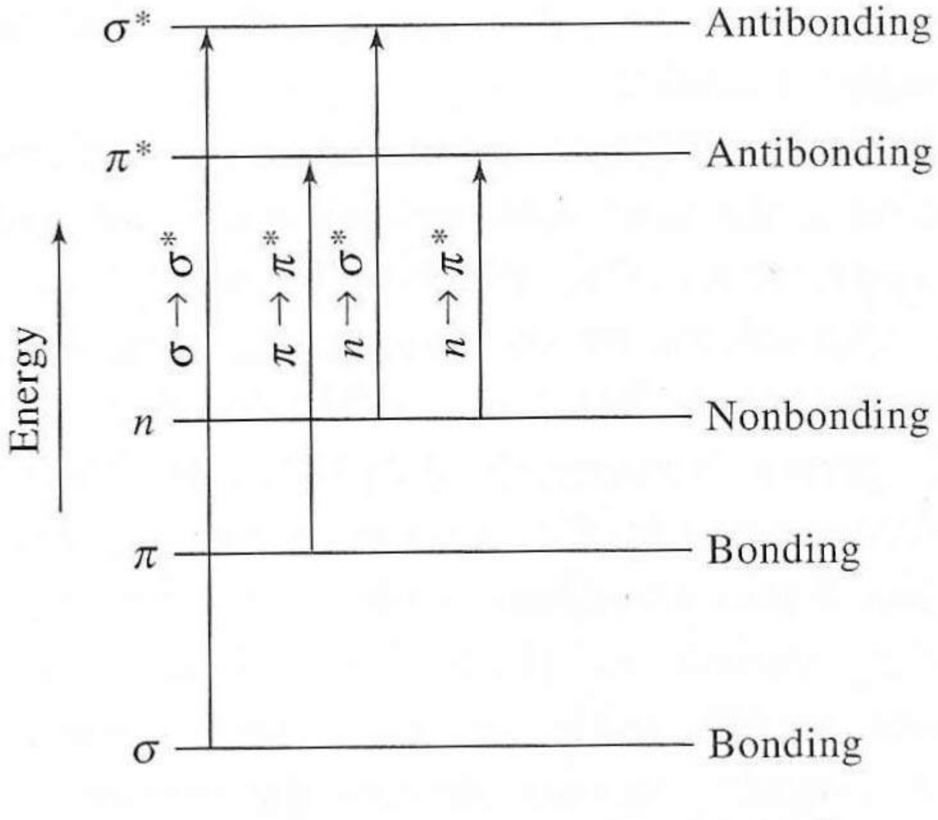


Figure 14-3 Electronic molecular energy levels.

Theory for UV/vis Spectrometry

σ → σ* 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 → σ* Transitions

- Occur in compounds containing atoms with unshared electrons.
- Absorption region 150 to 250 nm

Theory for UV/vis Spectrometry

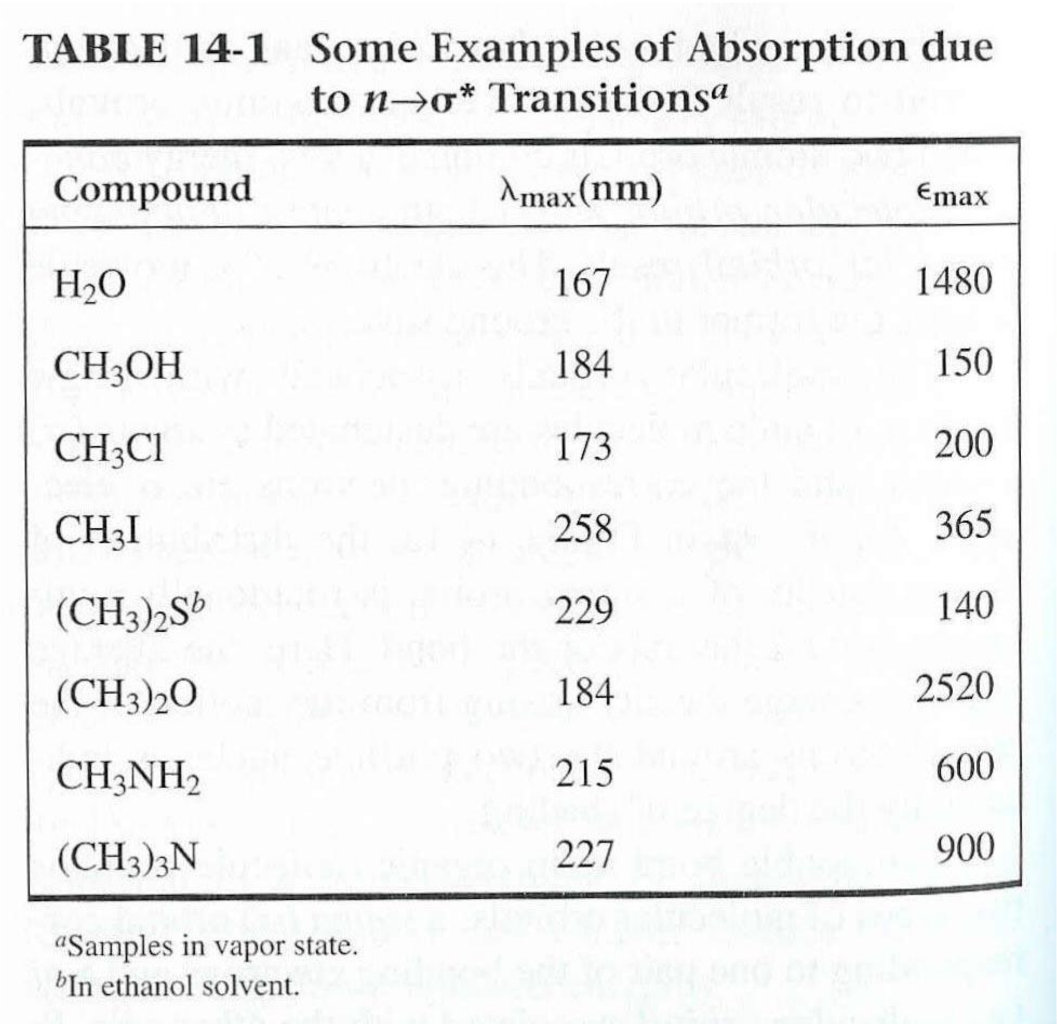


TABLE 14-1 Some Examples of Absorption due to $n \rightarrow \sigma^*$ Transitions[a]

Compound	λ_{max}(nm)	ϵ_{max}
H_2O	167	1480
CH_3OH	184	150
CH_3Cl	173	200
CH_3I	258	365
$(CH_3)_2S$[b]	229	140
$(CH_3)_2O$	184	2520
CH_3NH_2	215	600
$(CH_3)_3N$	227	900

[a] Samples in vapor state.

[b] In 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.

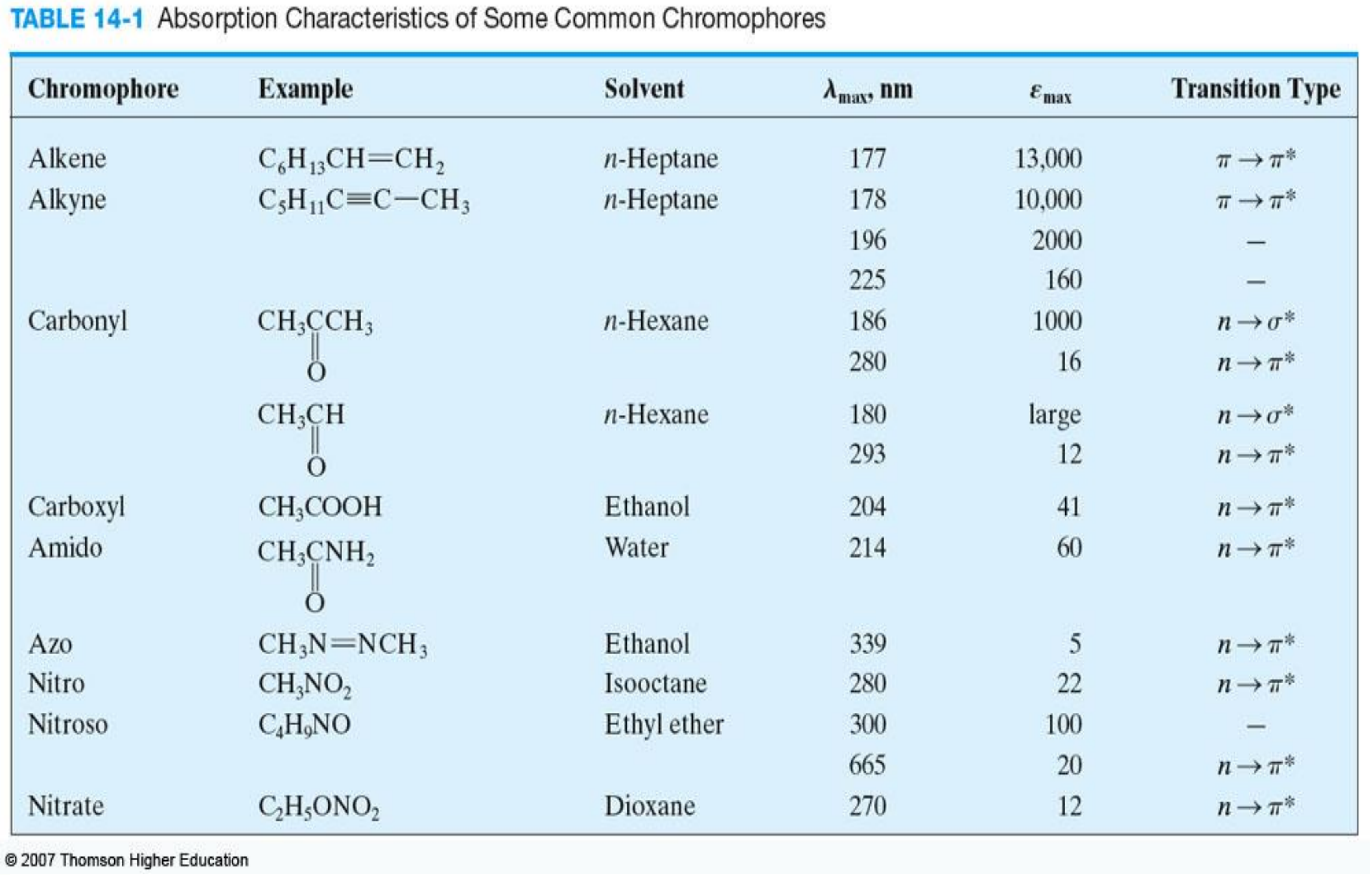


TABLE 14-1 Absorption Characteristics of Some Common Chromophores

Chromophore	Example	Solvent	λ_{max}, nm	ε_{max}	Transition Type
Alkene	$C_6H_{13}CH{=}CH_2$	*n*-Heptane	177	13,000	$\pi \rightarrow \pi^*$
Alkyne	$C_5H_{11}C{\equiv}C{-}CH_3$	*n*-Heptane	178	10,000	$\pi \rightarrow \pi^*$
			196	2000	–
			225	160	–
Carbonyl	$CH_3\underset{\underset{O}{\|}}{C}CH_3$	*n*-Hexane	186	1000	$n \rightarrow \sigma^*$
			280	16	$n \rightarrow \pi^*$
	$CH_3\underset{\underset{O}{\|}}{C}H$	*n*-Hexane	180	large	$n \rightarrow \sigma^*$
			293	12	$n \rightarrow \pi^*$
Carboxyl	CH_3COOH	Ethanol	204	41	$n \rightarrow \pi^*$
Amido	$CH_3\underset{\underset{O}{\|}}{C}NH_2$	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 → π* transitions to shorter λ's (blue shift).
- Shifts π → π* 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

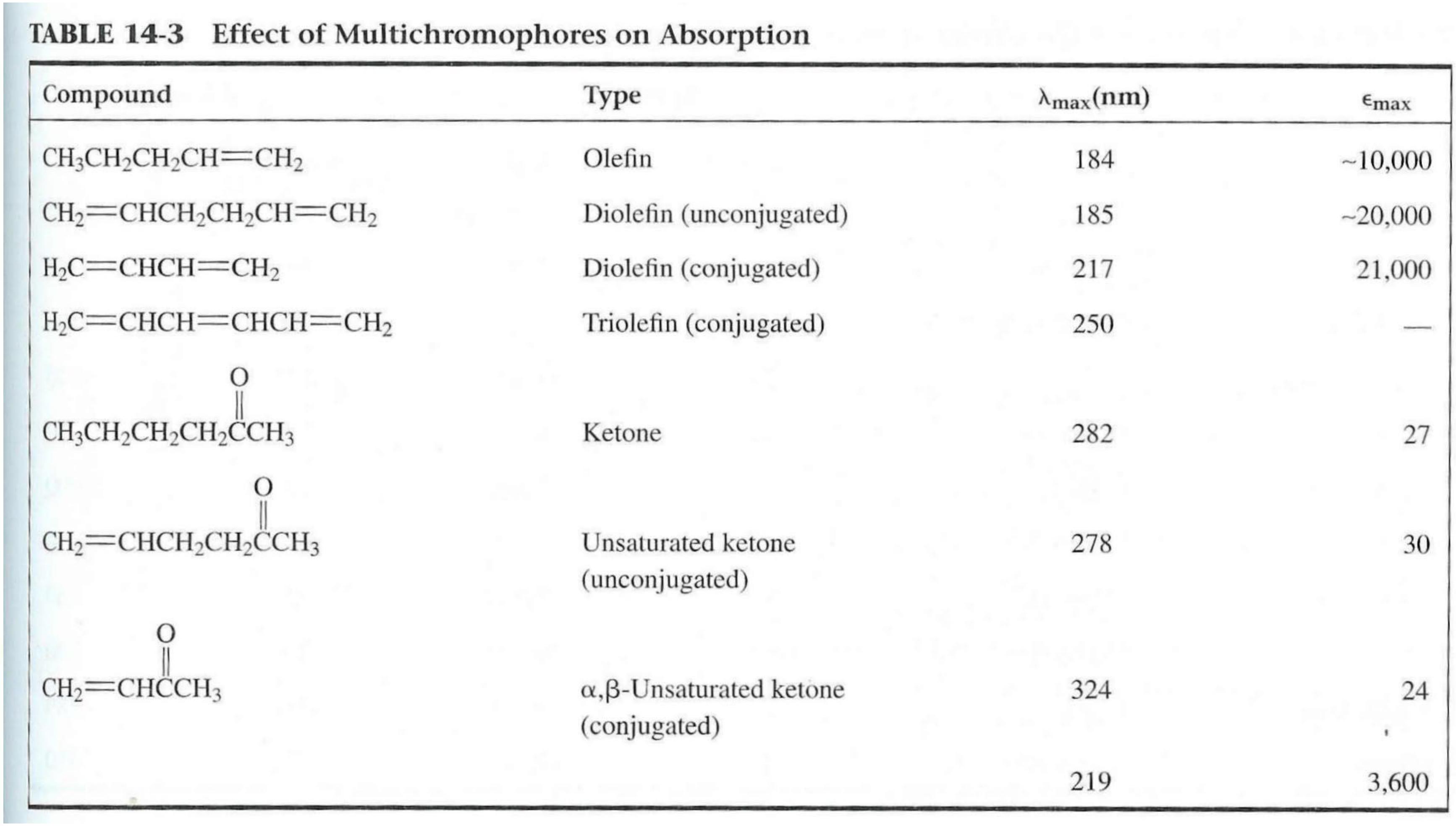


TABLE 14-3 Effect of Multichromophores on Absorption

Compound	Type	λ_{max}(nm)	ϵ_{max}
$CH_3CH_2CH_2CH{=}CH_2$	Olefin	184	~10,000
$CH_2{=}CHCH_2CH_2CH{=}CH_2$	Diolefin (unconjugated)	185	~20,000
$H_2C{=}CHCH{=}CH_2$	Diolefin (conjugated)	217	21,000
$H_2C{=}CHCH{=}CHCH{=}CH_2$	Triolefin (conjugated)	250	—
$CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$	Ketone	282	27
$CH_2{=}CHCH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$	Unsaturated ketone (unconjugated)	278	30
$CH_2{=}CH\overset{O}{\overset{\|}{C}}CH_3$	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-defines peaks and are not affected by environment (shielding of f electrons).

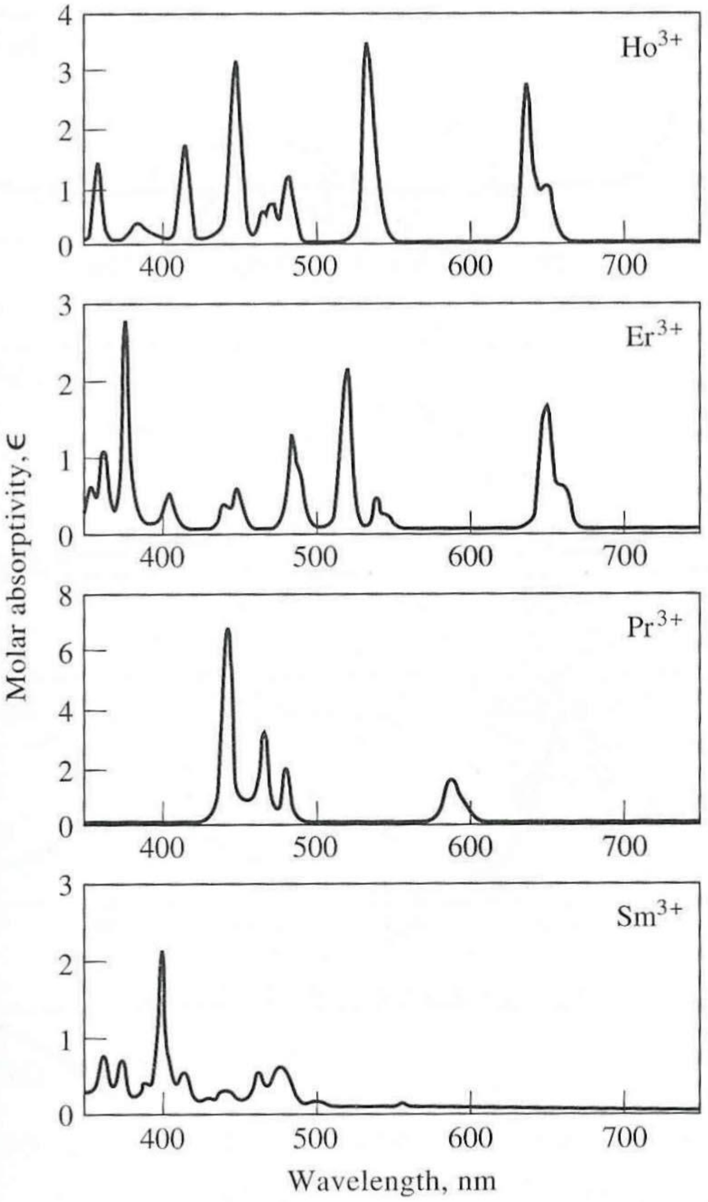


Figure 14-6 Typical absorption spectra for lanthanide ions.

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

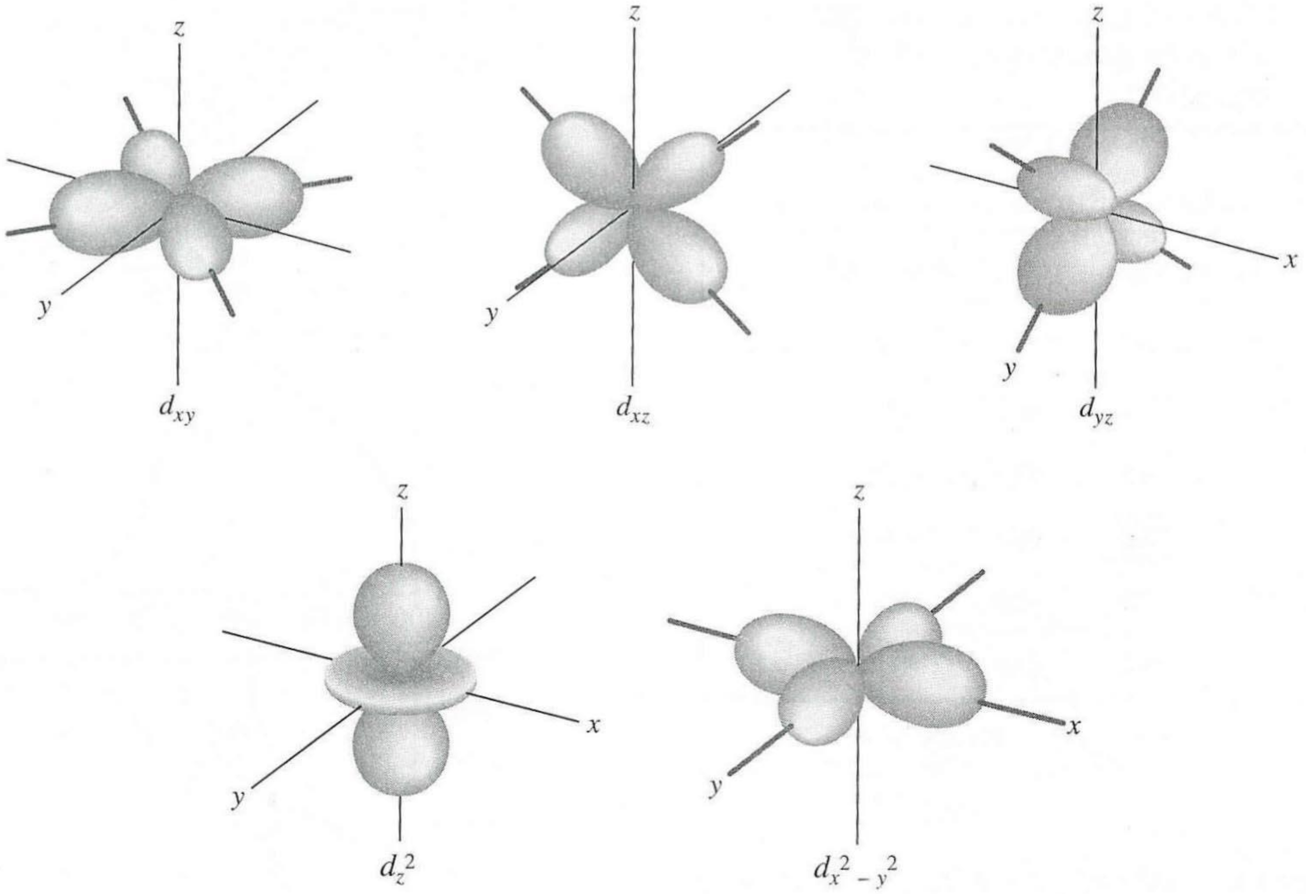


Figure 14-8 Electron-density distribution in the five *d* orbitals.

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_{z2} and d_{x2-y2} 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

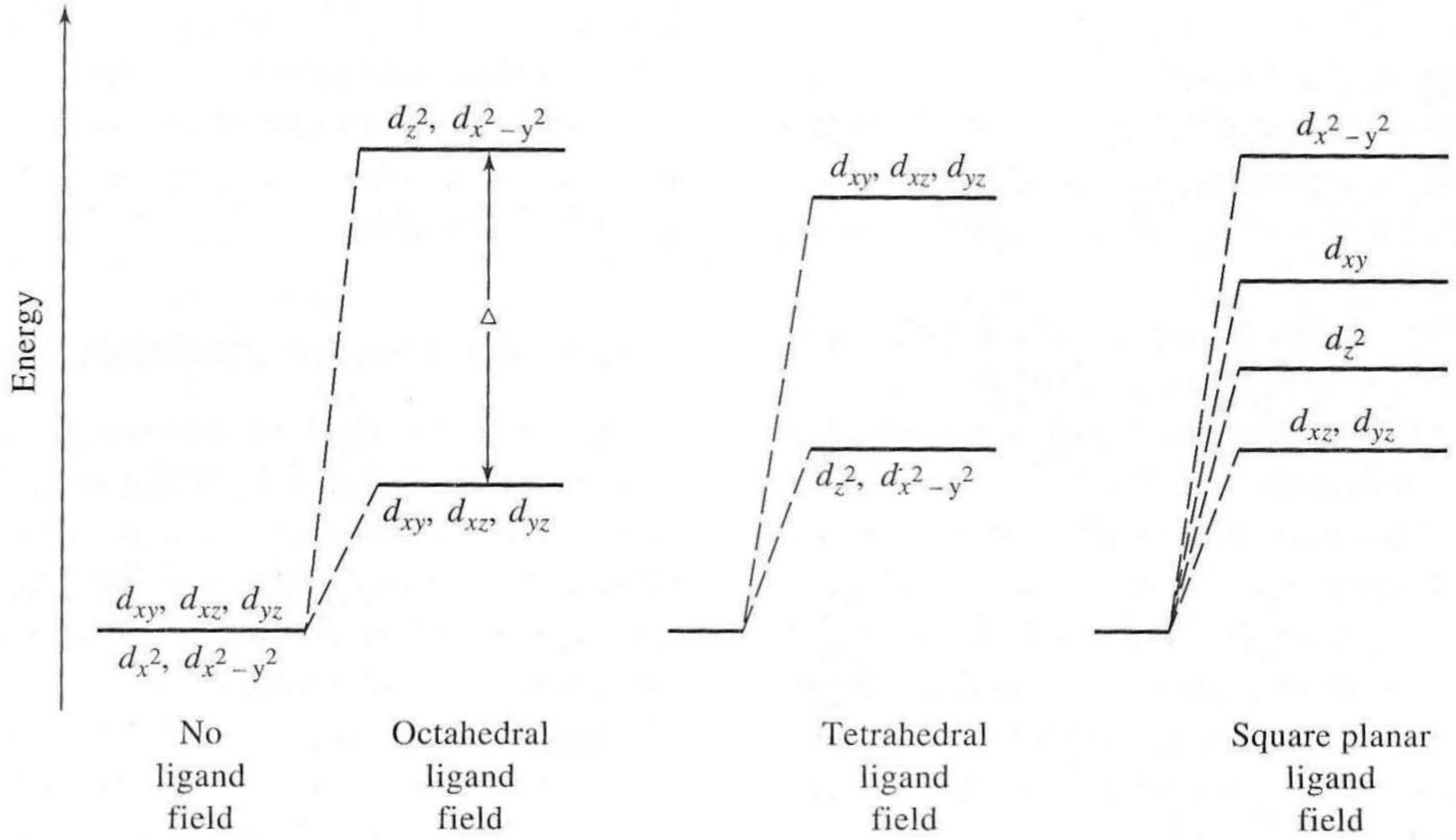


Figure 14-9 Effect of ligand field on *d*-orbital energies.

Theory for UV/vis Spectrometry

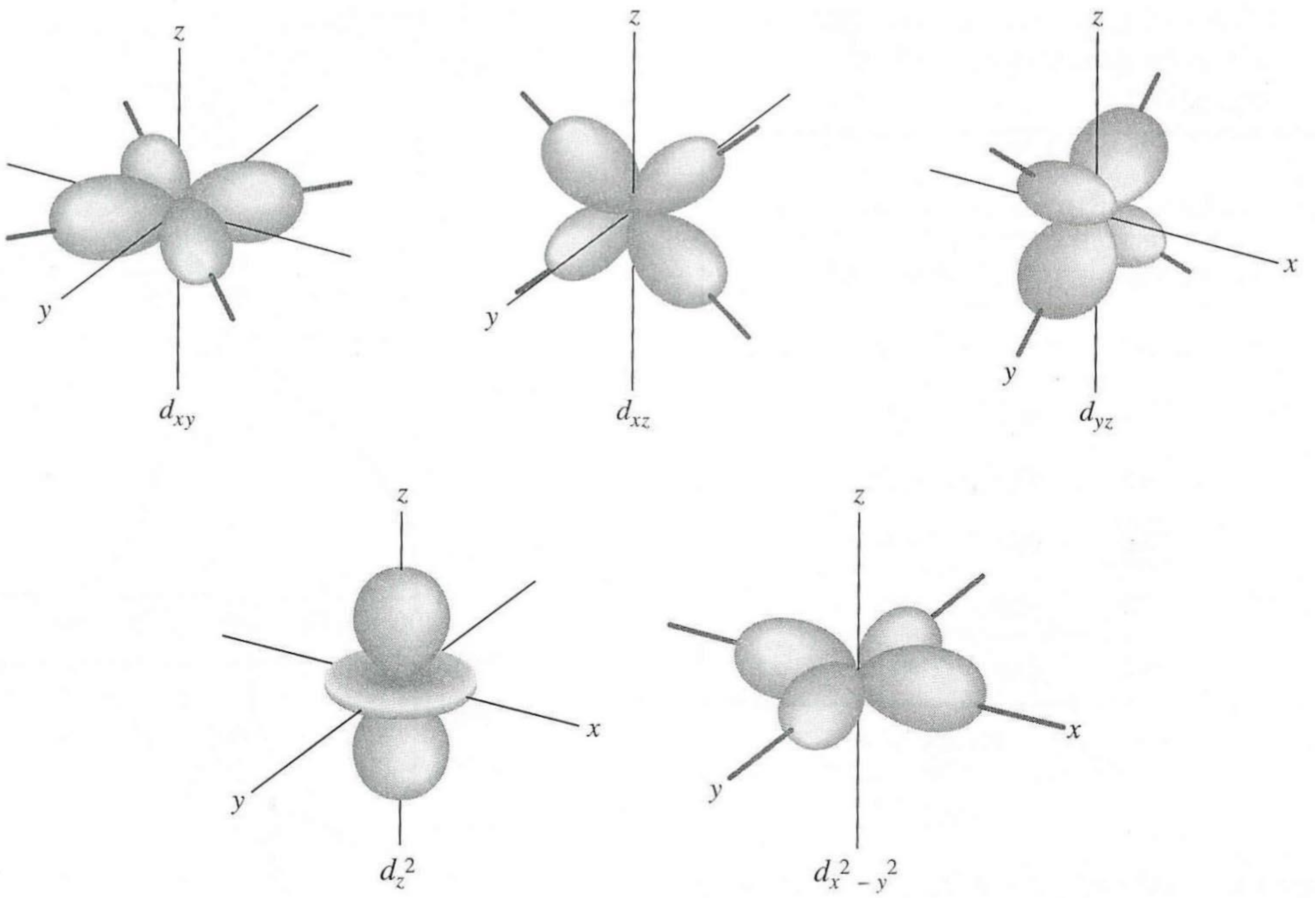


Figure 14-8 Electron-density distribution in the five *d* orbitals.

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

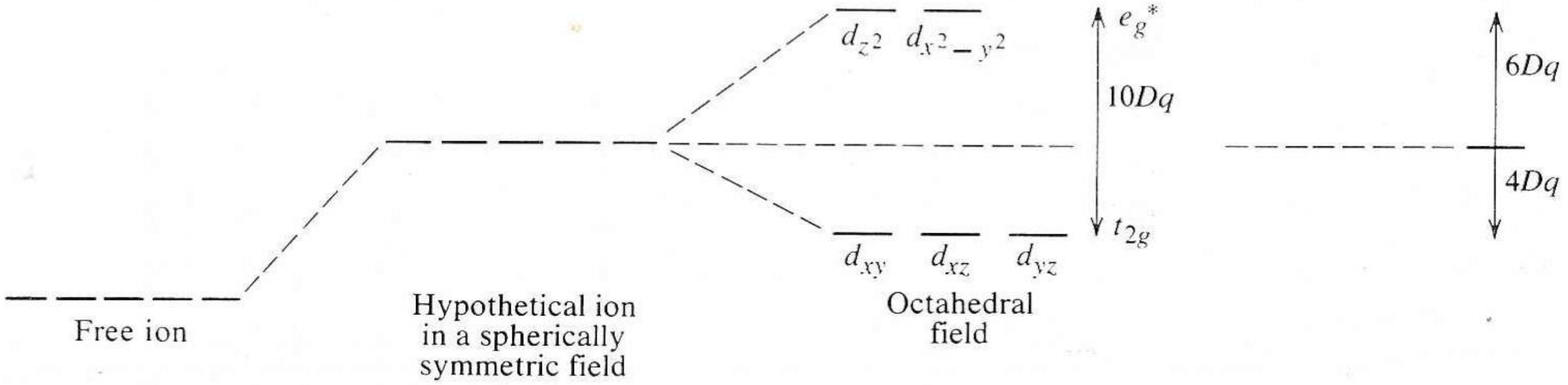


Figure 7.8 Splitting of the *d* energy levels in an octahedral complex.

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

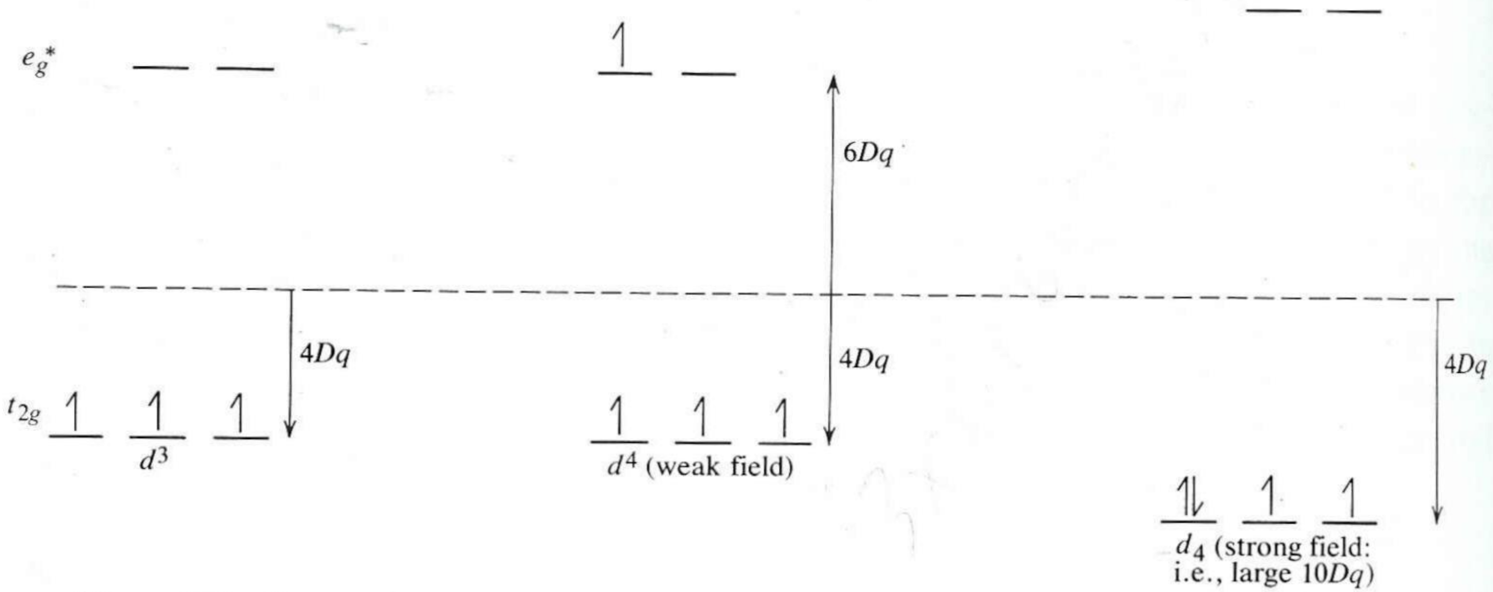


Figure 7.9 Occupation of *d* orbitals in octahedral complexes for d^3 and d^4 configurations.

Theory for UV/vis Spectrometry

Crystal field theory

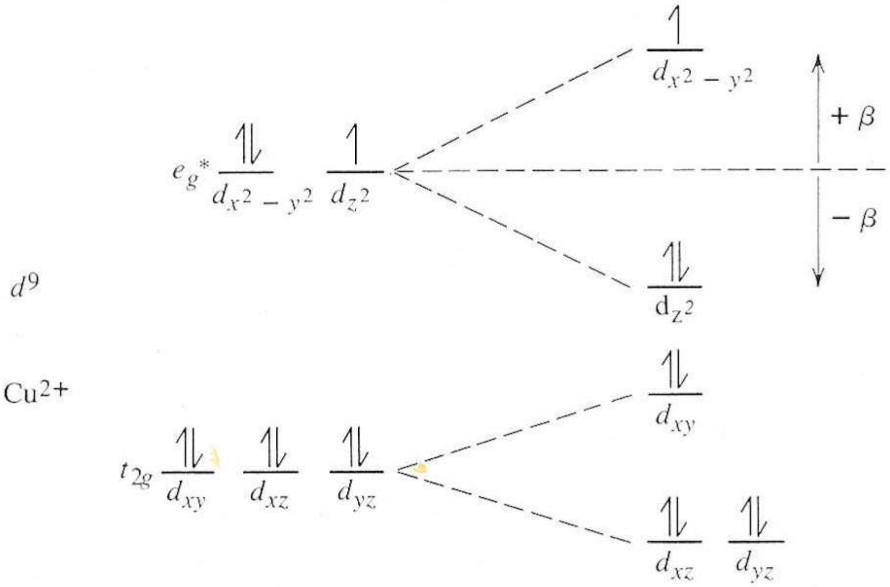


Figure 7.10 Splitting of the energy levels in an octahedral (tetragonal) field elongated along the *z* direction.

Theory for UV/vis Spectrometry

Crystal field theory

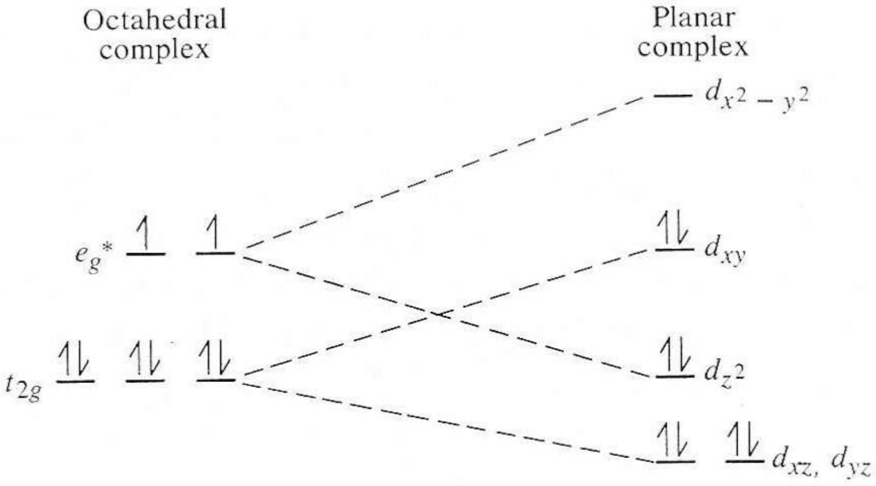


Figure 7.11 Energy levels for square planar nickel(II) complexes.

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

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

Theory for UV/vis Spectrometry

Ligand field strength

$I^- < Br^- < Cl^- < F^- < OH^- < C_2O_4^{2-} \sim H_2O < SCN^- < NH_3 <$ ethylenediamine $<$ 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

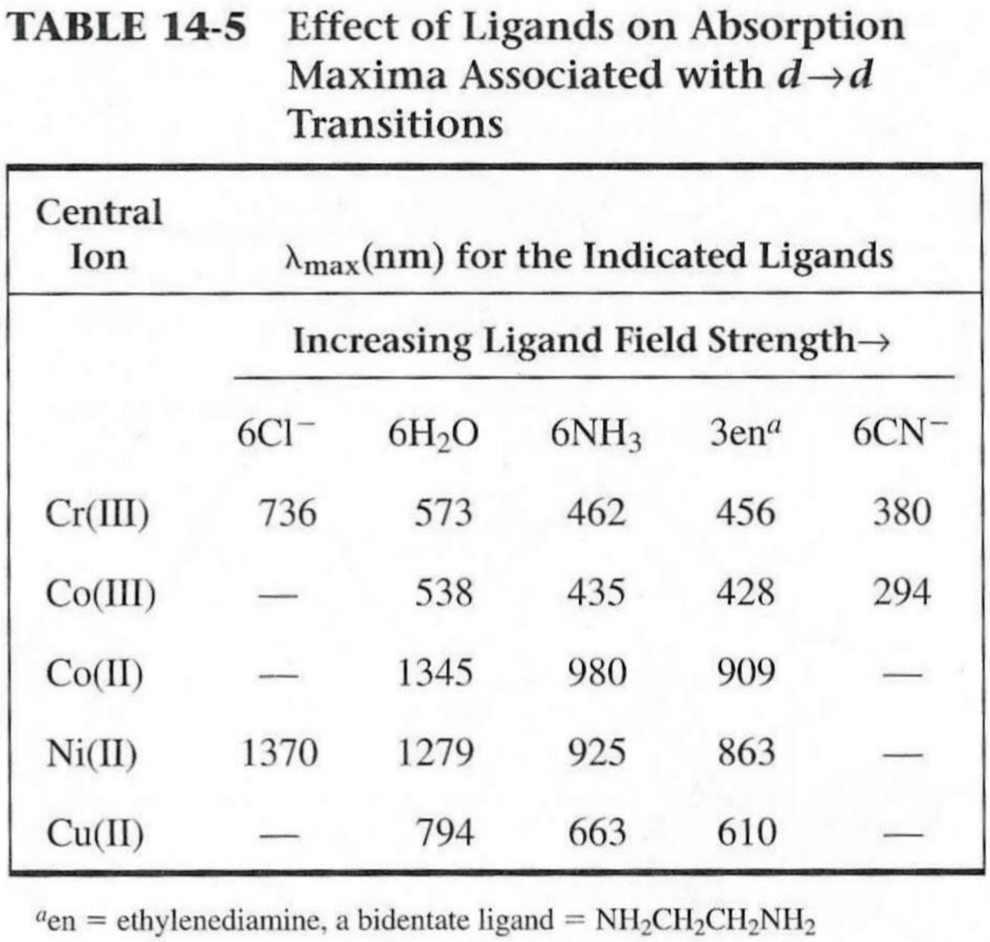


TABLE 14-5 Effect of Ligands on Absorption Maxima Associated with $d \rightarrow d$ Transitions

Central Ion	λ_{max}(nm) for the Indicated Ligands				
	Increasing Ligand Field Strength→				
	$6Cl^-$	$6H_2O$	$6NH_3$	$3en^a$	$6CN^-$
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	—

[a] en = ethylenediamine, a bidentate ligand = $NH_2CH_2CH_2NH_2$

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 ($\varepsilon_{max} > 10{,}000$)

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

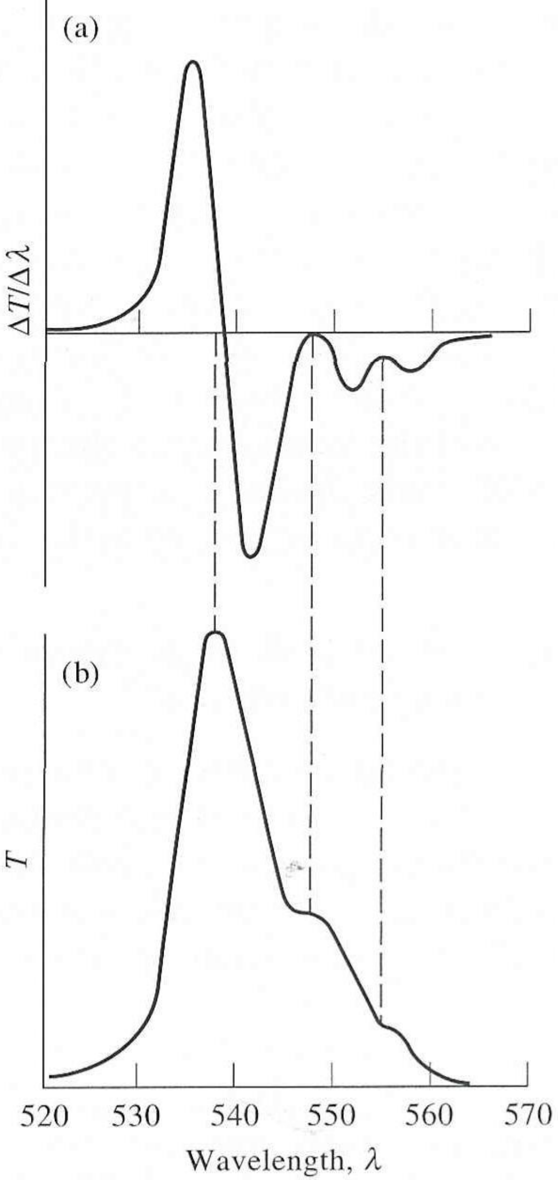


Figure 14-16 Comparison of a derivative spectrum (a) with a standard transmittance spectrum (b).

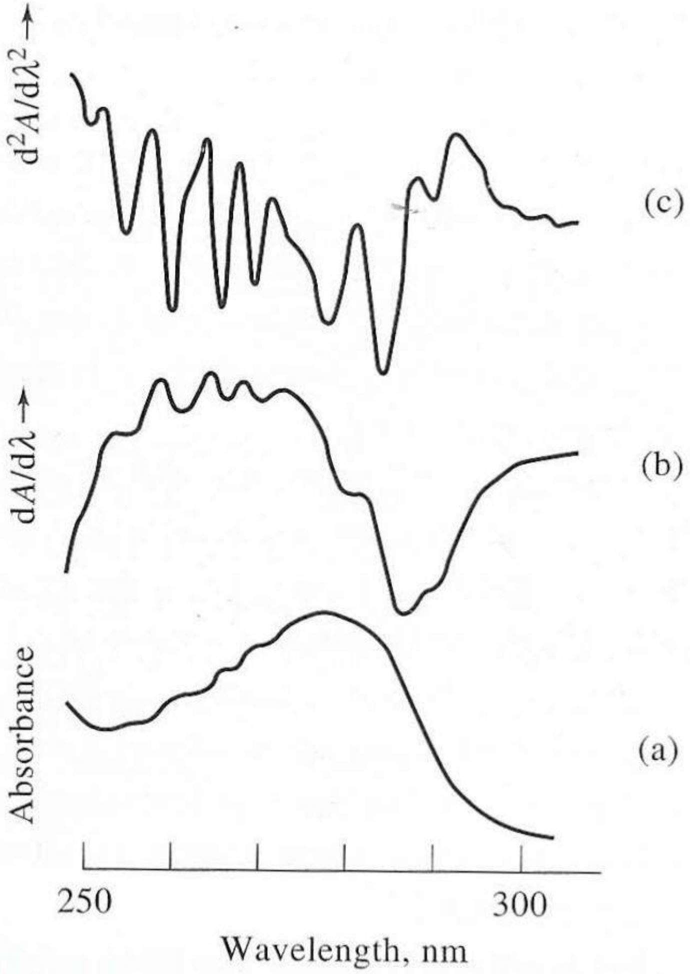


Figure 14-17 Absorption spectra of bovine albumin: (a) ordinary spectrum, (b) first derivative spectrum, (c) second derivative spectrum. *(Reprinted with permission from J. E. Cahill and F. G. Padera,* Amer. Lab., ***1980****,* 12*(4), 109. Copyright 1980 by International Scientific Communications, Inc.).*

Assignment

- Read Chapters 15, 16, and 17