84.514
Advanced Analytical Chemistry

Part III
Molecular Spectroscopy (continued)

Website

http://faculty.uml.edu/David_Ryan/84.514

http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/UV-Vis/spectrum.htm

Molecular Absorption in UV-vis Region

Practical considerations – discussion limited to species absorbing at λ's > 200 nm. Work below 200 nm is extremely difficult because:

1) O_2 absorbs starting at ~195 nm & below
2) N_2 absorbs starting at ~145 nm & below
3) H_2O absorbs starting at ~178 nm & below
4) Crystalline quartz absorbs below ~185 nm
5) Amorphous quartz absorbs below ~170 nm
6) CaF_2 & LiF only suitable optical materials

7) Few good sources – rare gas discharge lamps

8) Generally there is very little spectroscopic information available below 200 nm & its not worth the trouble

Region below 200 nm is known as the **vacuum UV** because one approach to work in this region is to evacuate the monochromator or purge it with a non absorbing gas like He or Ar

Region of interest is from 195 – 200 nm up to 650 – 800 nm

Theory – The total energy of a molecule can be broken down into several types of energy

For UV-vis must consider:

      electronic energy

      vibrational energy

      rotational energy

Ignore translational energy

Electronic energy involves changes in energy levels of the outer electrons of a molecule

- these changes correspond to the energy of the ultraviolet-visible radiation

- these changes are quantized (i.e. discrete levels exist corresponding to quanta of light)

$$\Delta E \ = \ \Delta E_{elec.} \ + \ \Delta E_{vib.} \ + \ \Delta E_{rot.}$$

Energy change or transition for absorption

Largest energy

Smallest energy

Simplified Energy Level Diagram

E

Vibrational Levels (4)

Electronic Levels (2)

Rotational Levels (5)
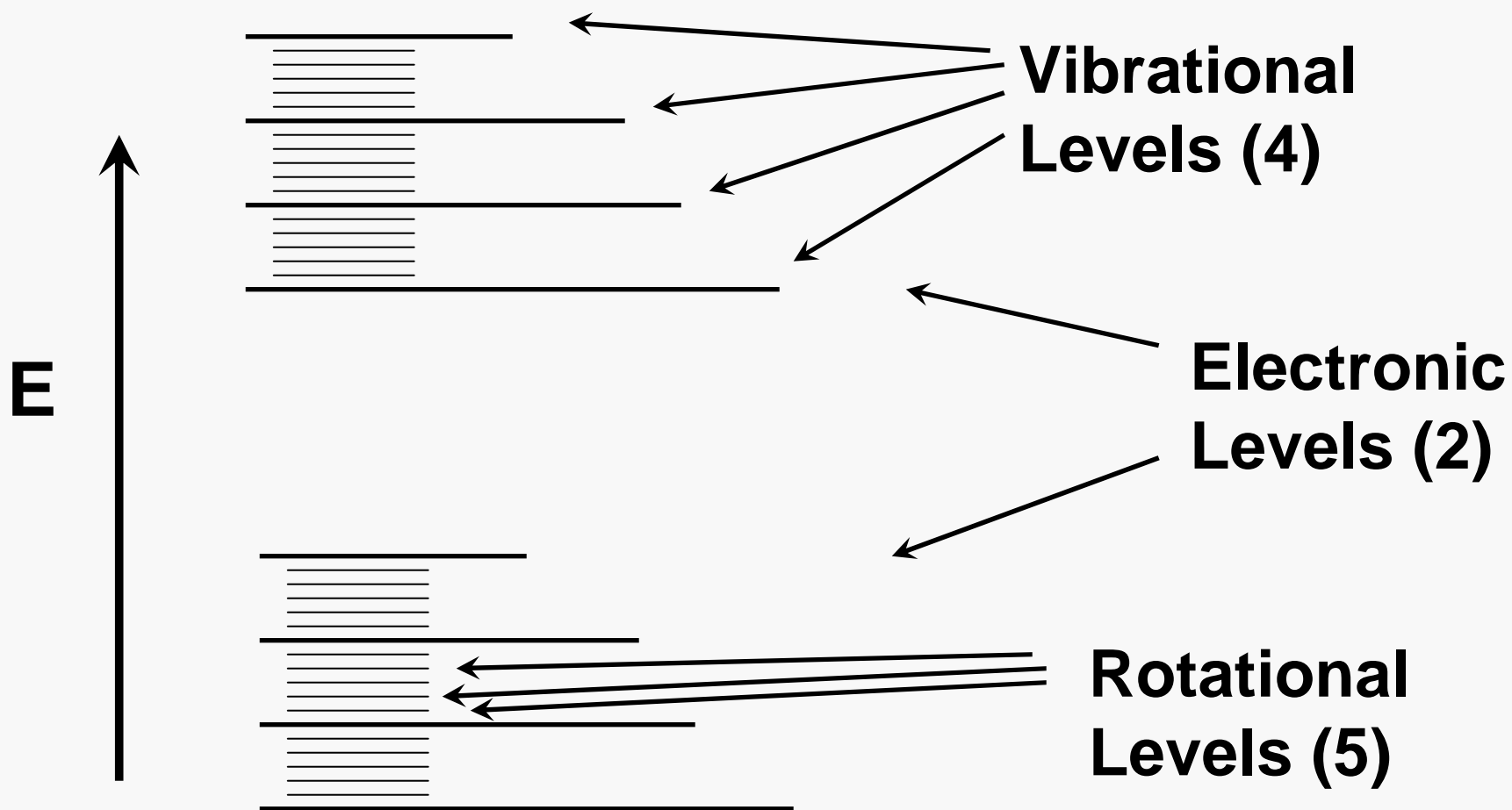
For an unperturbed molecule in the gas phase (low pressure) the absorption spectrum would be a series of lines somewhat closely spaced together. However, molecules are usually under the influence of other molecules → energy levels are perturbed → get broadening and overlap of spectral lines (same idea as with continuum sources).
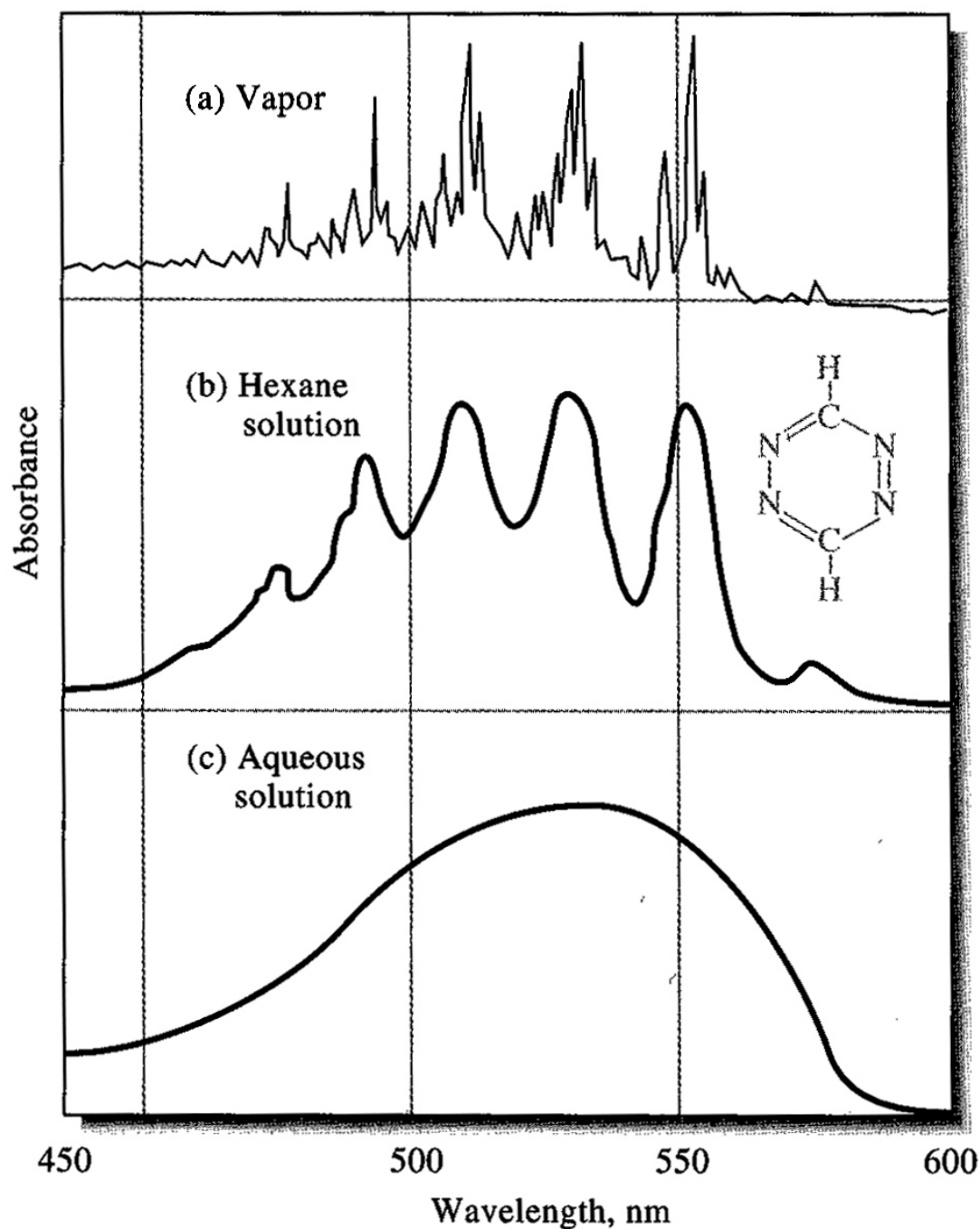
Tetrazine absorption spectrum under various conditions

Vapor phase spectrum gives greatest fine structure

In hexane solution many features are lost due to tetrazine interactions with the solvent

In aqueous solution all spectral features are lost & all peaks merge into one

The "smearing out" effect is greater in the liquid phase than in gas phase:

- In gas phase it increases with pressure

- In liquid phase it increases with the degree of solvation of the molecule

(polar solvents always interact more with molecules)

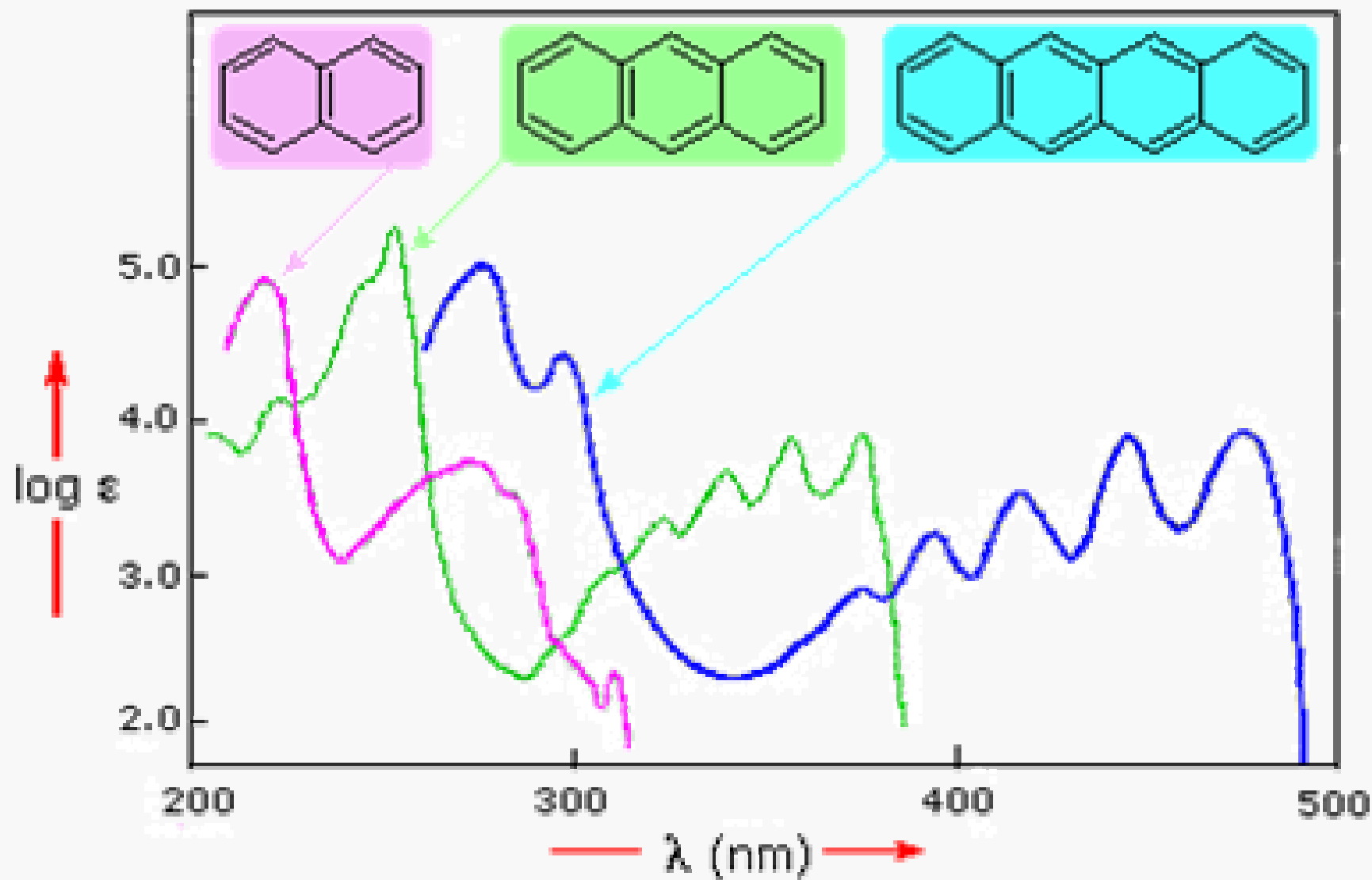Some molecules inherently interact less with solvents so spectra have more features

Rigid molecules like PAHs interact less with solvents & therefore have more features

Polyaromatic Hydrocarbon (PAH) spectra

Naphthalene   Anthracene   Tetracene

Molar Absorptivity or Absorption Probabilities

ε is a measure of, or can be thought of as absorption probability – specific for a wavelength and therefore a transition

In general

$\varepsilon = 10^4$ to 10^5 $\rightarrow$ highly probable transition
(very strong absorption)

$\varepsilon = 10^3$ to 10^4 $\rightarrow$ strong absorption

$\varepsilon < 10^3$ $\rightarrow$ weak absorption

Organic Molecules – Structure & Absorption

Atomic orbital combine to give molecular orbitals

Two types of orbitals:

- **bonding orbitals** – more stable than atomic orbitals (lower energy)

- **antibonding orbitals** – less stable than atomic orbitals (higher energy) – denoted by *

Two types of bonds:

- σ = **sigma bonds** formed by s orbital overlap – no nodal plane – stable – electrons associated with one or two nuclei

- π = **pi bonds** formed by p orbital hybridization – one nodal plane – only in unsaturated compounds – multiple π bonds leads to conjugation → delocalization of electrons → electrons not tightly held & spread out over many nuclei

Must also consider electrons that are not involved in bonds, e.g. C=O has two pairs of electrons on the oxygen = **non bonded electrons (n electrons)** – present when heteroatom is present (N, S, O, S, etc.)

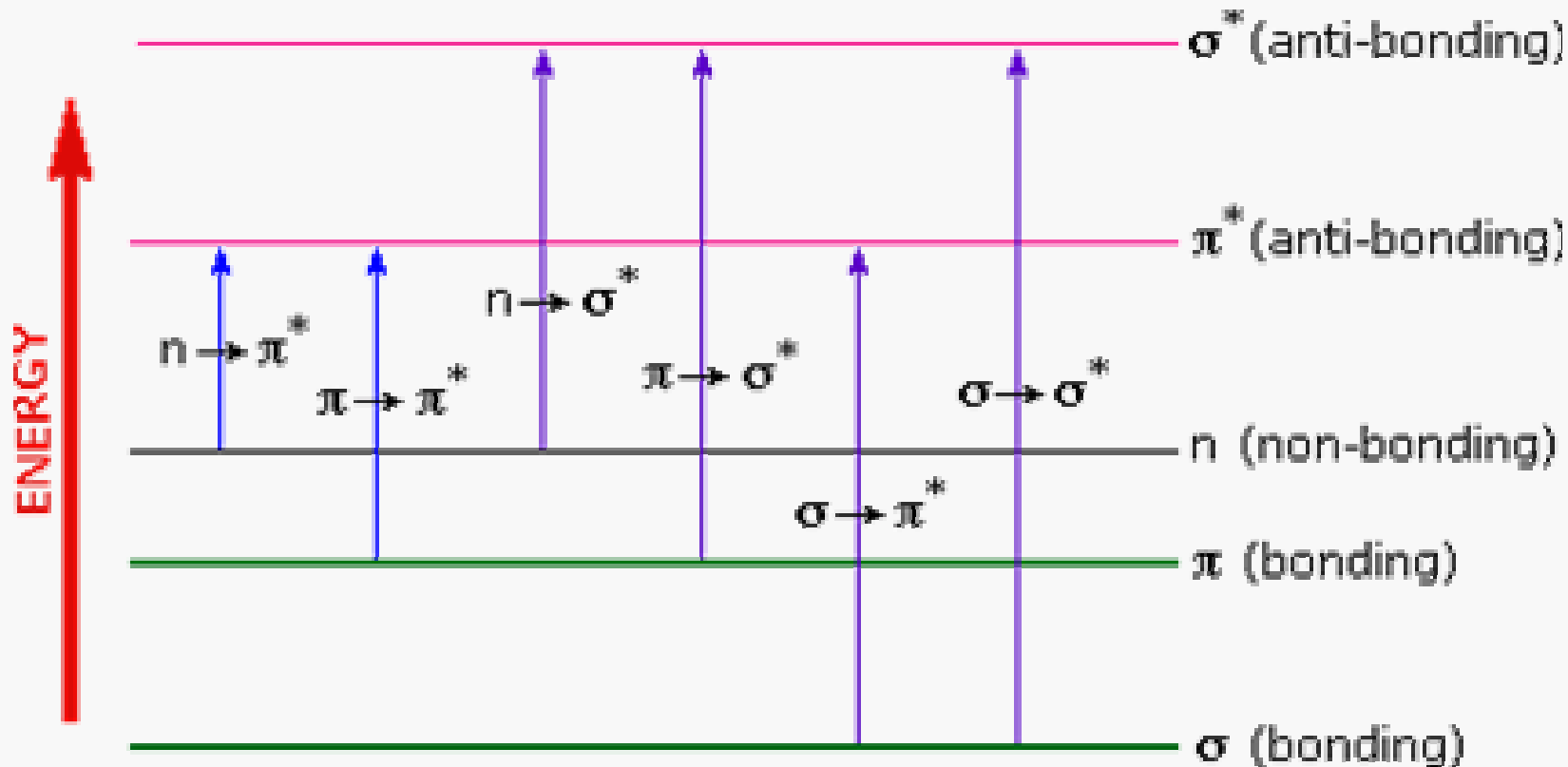Bonding orbitals are filled, antibonding orbitals are empty
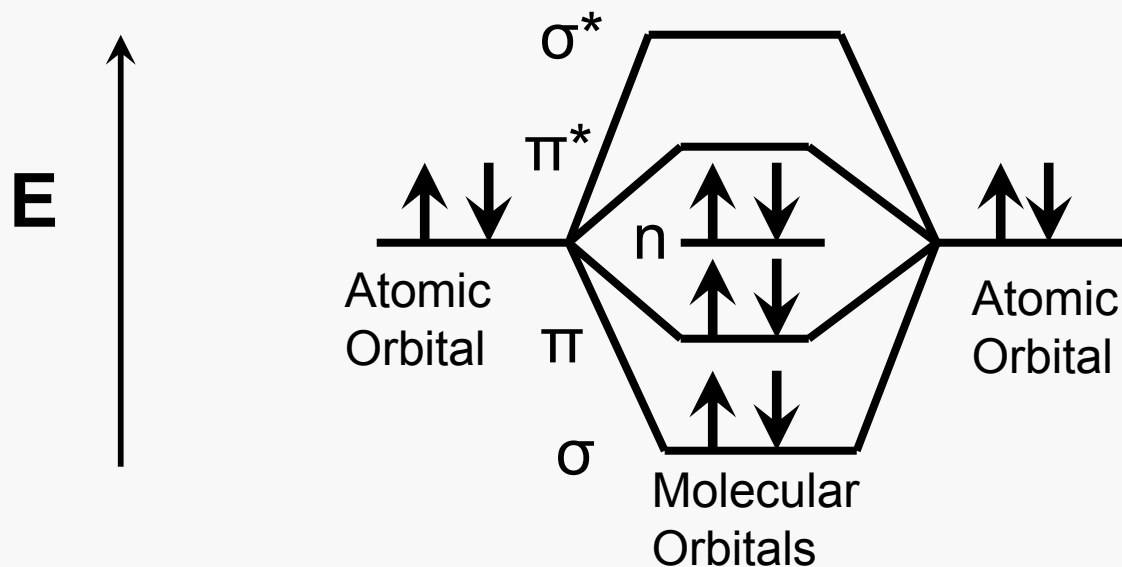
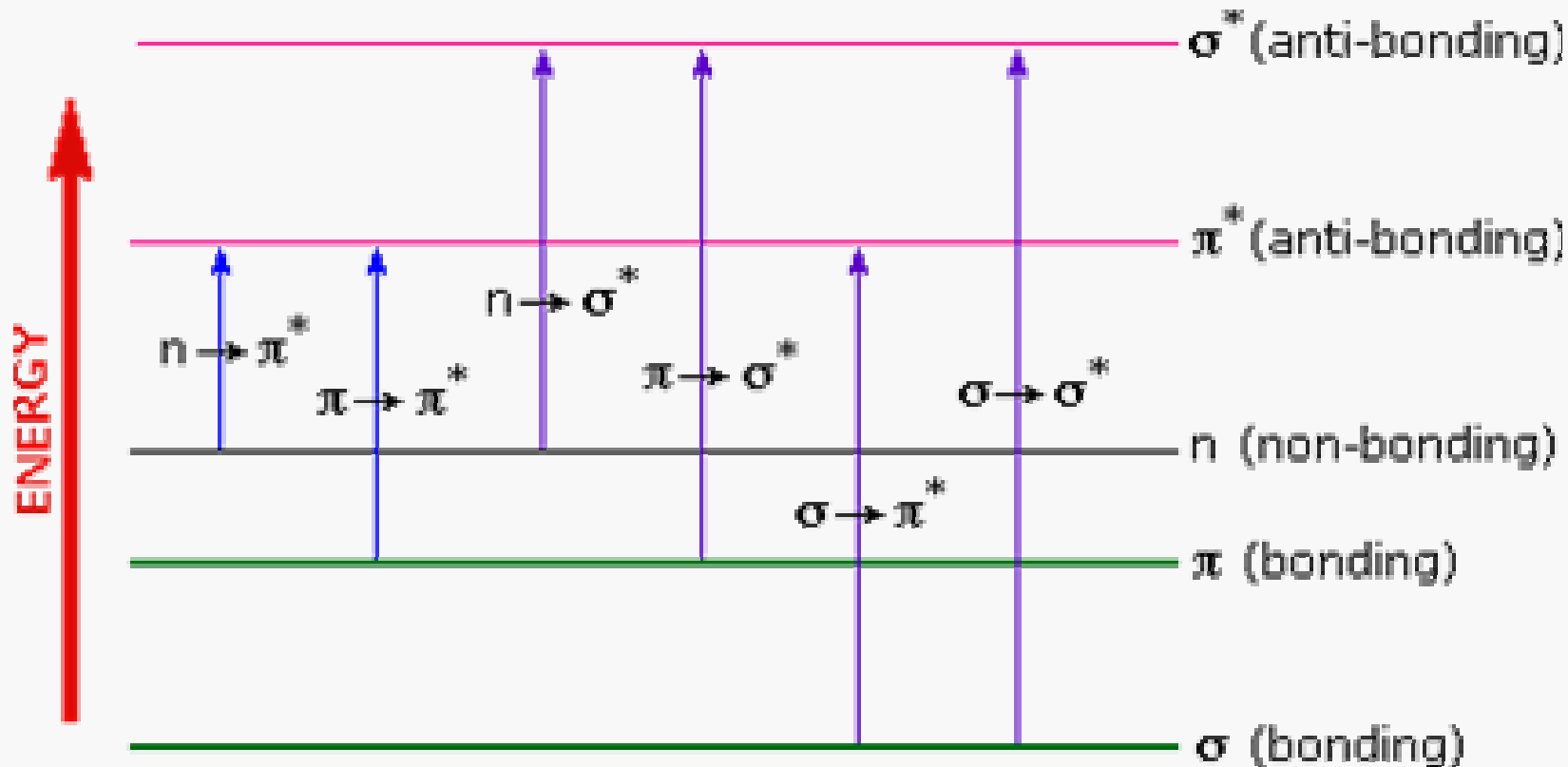When absorption occurs, electrons are promoted to * or antibonding orbitals

Another view of molecular orbitals and the possible electronic transitions
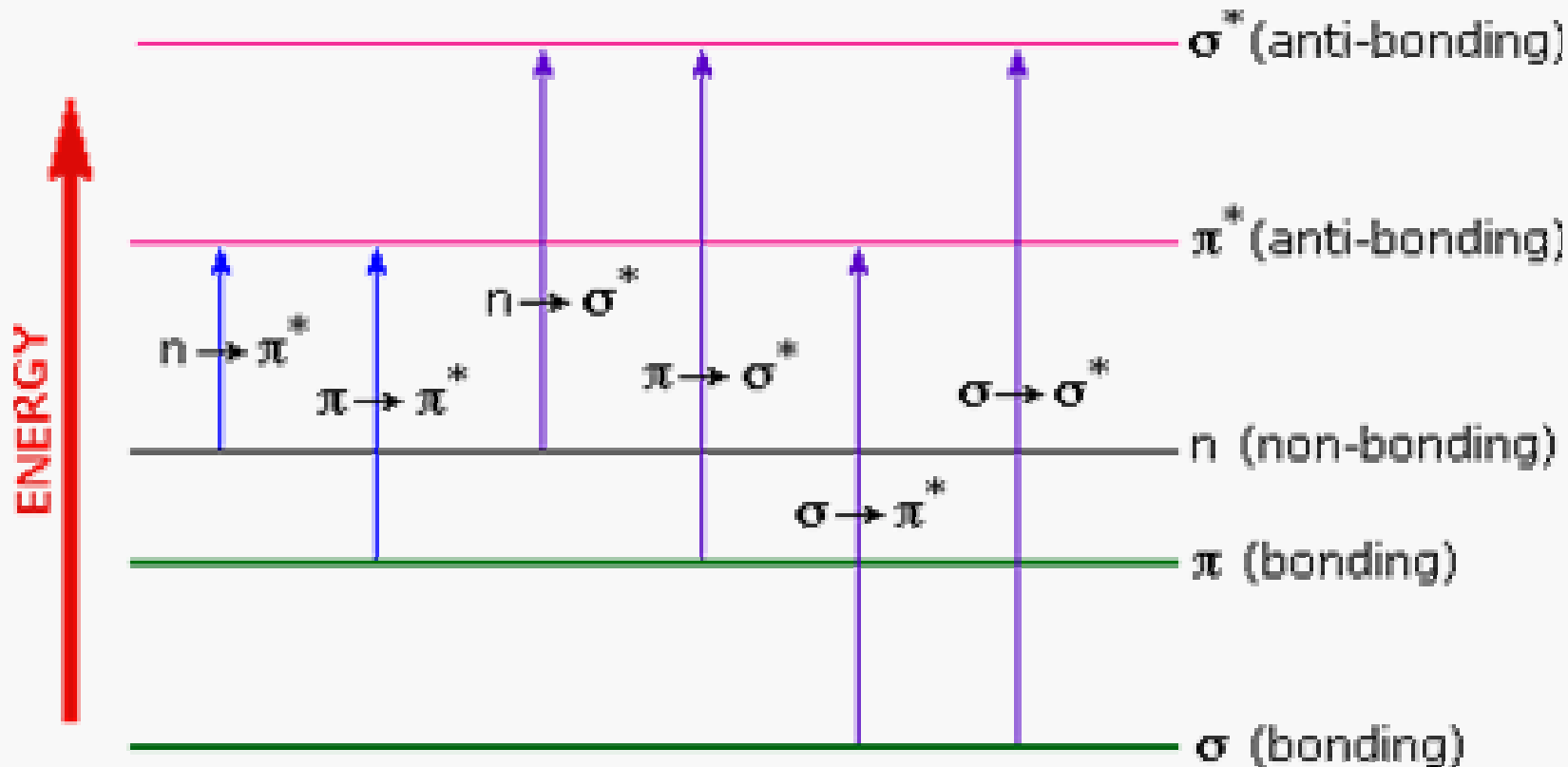
Note energy gaps for different transitions
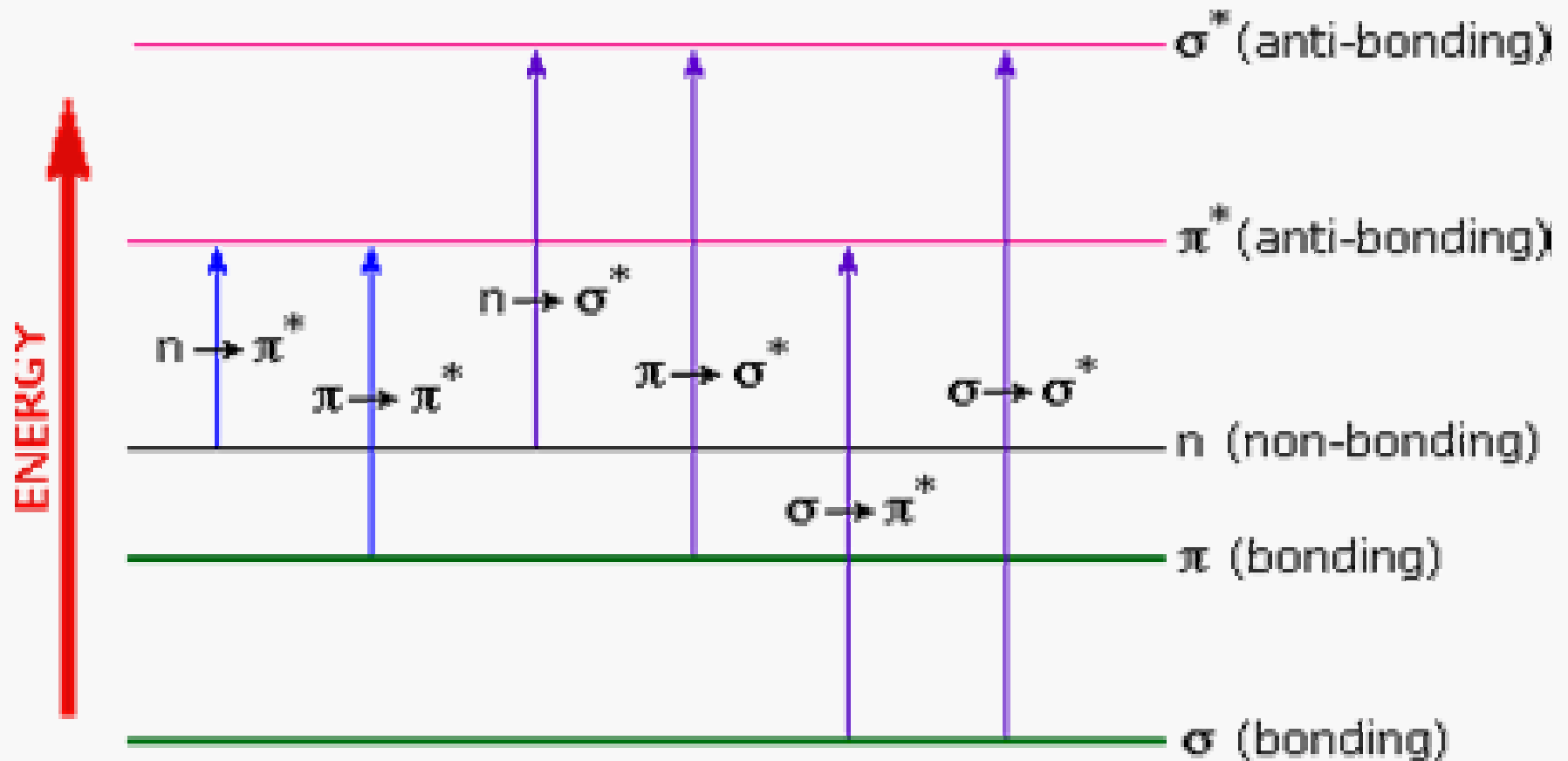
Energy difference between π & π* levels is relatively small therefore π-π* transitions are usually observable

σ-σ* transitions are high energy transitions → occur at short λ's i.e. below 200 nm and are neither easily accessible or of great importance (vacuum UV)

n-π* transitions are observed in saturated compounds containing heteroatoms (n electrons), ε usually low (10^3 – 10^2) because there is very little overlap between the two orbitals

Chromophore	Example	Excitation	λ_{max}, nm	ε	Solvent
C=C	Ethene	$\pi \rightarrow \pi^*$	171	15,000	hexane
C≡C	1-Hexyne	$\pi \rightarrow \pi^*$	180	10,000	hexane
C=O	Carbonyl	$n \rightarrow \pi^*$	290	15	hexane
		$\pi \rightarrow \pi^*$	180	10,000	hexane
N=O	Nitromethane	$n \rightarrow \pi^*$	275	17	ethanol
		$\pi \rightarrow \pi^*$	200	5,000	ethanol
C-X X=Br	Methyl bromide	$n \rightarrow \sigma^*$	205	200	hexane
X=I	Methyl Iodide	$n \rightarrow \sigma^*$	255	360	hexane

Larger heteroatoms e.g. I vs Br vs Cl have n-σ* transitions at longer λ's since larger atoms have less of a grip on outer electrons so n electrons easily promoted

Sulfide electrons more easily promoted than oxygen

Br and I electrons are more easily promoted than Cl

TABLE 2-6 Absorption·Wavelength and Intensity Due to $n \rightarrow \sigma^*$ Transitions of Some Saturated Molecules Containing Heteroatoms†

Heteroatom	Compound	λ_{max}, nm	ϵ_{max}
—Cl	CH_3Cl	173	200
—O	CH_3OH	184	150
—Br	CH_3Br	204	200
	$n\text{-}PrBr$‡	208	320
—I	CH_3I	259	365
	CH_2I_2	202	1320
	CHI_3	349	230
—N	CH_3NH_2	215	600
	$(CH_3)_3N$	227	820
—S	$(CH_3)_2S$	210	1020
	Et_2S‡	215	1600
—S—S—			
Acyclic	$C_2H_5SSC_2H_5$	202	2100
In six-membered ring	Tetramethyl disulfide	295	300
In five-membered ring	Trimethyl disulfide	334	180

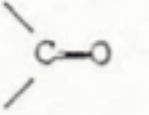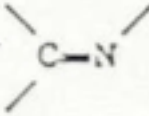# Some Examples of Absorption Due to $n \rightarrow \sigma^*$ Transitions
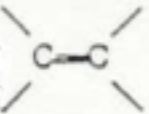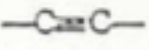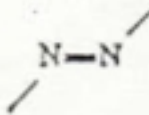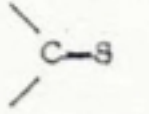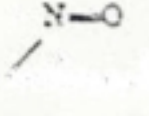
Compound	λ_{max}(nm)	ϵ_{max}
H_2O	167	1480
CH_3OH	184	150
CH_3Cl	173	200
CH_3I	258	365
$(CH_3)_2S$	229	140
$(CH_3)_2O$	184	2520
CH_3NH_2	215	600
$(CH_3)_3N$	227	900

n-π* transitions generally occur in accessible regions of spectrum (i.e. UV-vis)

Difference between O and N is that O is more electronegative so it holds onto n electrons better

n electrons of S in C=S more easily promoted than n electrons of N in N=N or C=N (i.e. 500 nm is lower energy)

TABLE 2-1 Absorption Maxima for $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ Transitions of Some Isolated Functional Groups

Functional group	Transition, nm	
	$\pi \rightarrow \pi^*$ (intense absorption)	$n \rightarrow \pi^*$ (weak absorption)
C=C	170	None
—C≡C—	170	None
C=O	166	280
C=N	190	300
N=N		340
C=S		500
N=O		665

Characteristics of n-π* and n-σ* transitions:

1) Weak absorption (ε usually between 100 & 1000 L/mol-cm). This is primarily due to overlap. n orbitals overlap only slightly with π* orbitals → probability of n electrons being in the right place for absorption is low

2) The less strongly the n electron is held (i.e. less electronegative and the larger the heteroatom) → the longer the absorption λ

3) For n-π* and n-σ* transitions the ground state is more polar than the excited state. Increasing solvent polarity → ground state is stabilized with respect to the excited state → larger ΔE → λ_{max} shifts to shorter λ (= hypsochromic effect or blue shift).
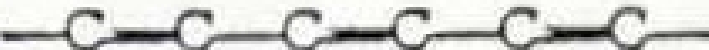

E

π*

n

ΔE
Larger

Non-polar solvent
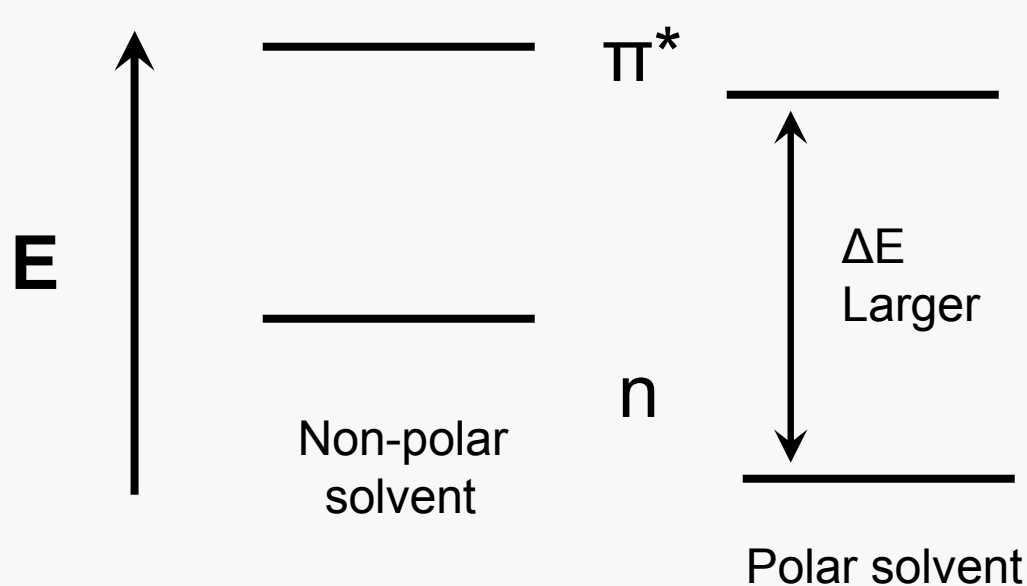
Polar solvent

Both energy levels are stabilized with more polar solvents but the ground state is affected more

Characteristics of π-π* transitions:

1) Large ε typically > 10^4 unless forbidden by selection rules

2) Less affected by nature of atoms comprising the π system (Table 2-1, π-π*) delocalization not very dependent on exact nature of atoms

3) As conjugation increases → λ_{max} gets longer and ε increases

TABLE 2-2   Approximate Absorption Maxima and Molar Absorptivity of $\pi \rightarrow \pi^*$ Transitions in Various Carbon–Carbon Bonds

Structure	λ_{max}, nm	ε
—C=C—	170	16,000
—C=C—C=C—	220	21,000
—C=C—C=C—C=C—	260	35,000

4) Excited state is generally more polar than the ground state (opposite of what happens with n-π*)

$$E \uparrow$$

π* ————

π ————

Non-polar solvent

————

————

ΔE Smaller
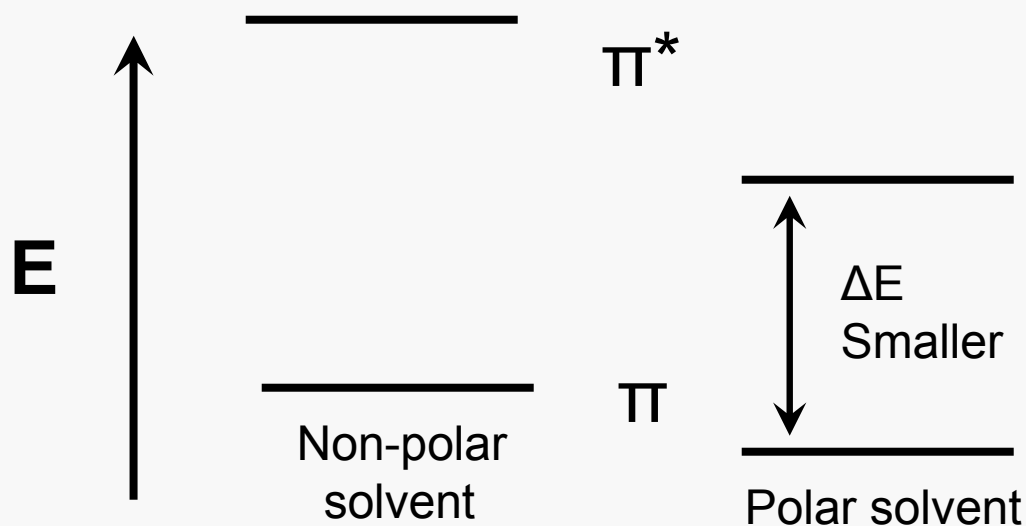
Polar solvent

Increased solvent polarity → excited state stabilized relative to ground state → smaller ΔE → λ_{max} shifts to longer λ

(= bathochromic shift or red shift)

Charge Transfer Absorption
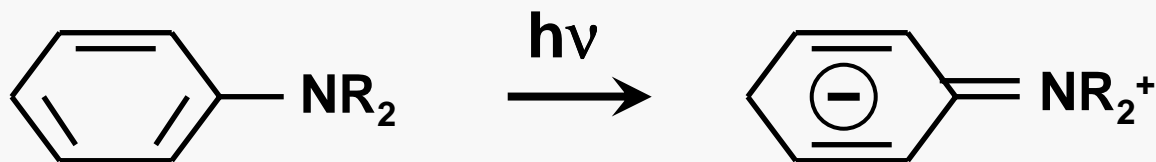
Observed for both organic & inorganic species

Typically two components to the absorbing species – one serves as an electron donor (D) & the other as an electron acceptor (A)

$$D \bullet A \; + \; h\nu \; \rightarrow \; D^+ \bullet A^-$$

Signifies an association of some type

$$h\nu \; = \; I_D \; + \; E_A \; - \; C$$

Energy of absorbed radiation

Ionization potential of donor, i.e. energy to pull electron away

Electron affinity of acceptor

Electrostatic energy of $D^+ \bullet A^-$ relative to $D \bullet A$ (Stabilized in polar solvent)

Examples

$$Fe^{3+} \bullet SCN^- \;+\; h\nu \;\rightarrow\; Fe^{2+} \bullet SCN$$

(thiocyanate)   A   D
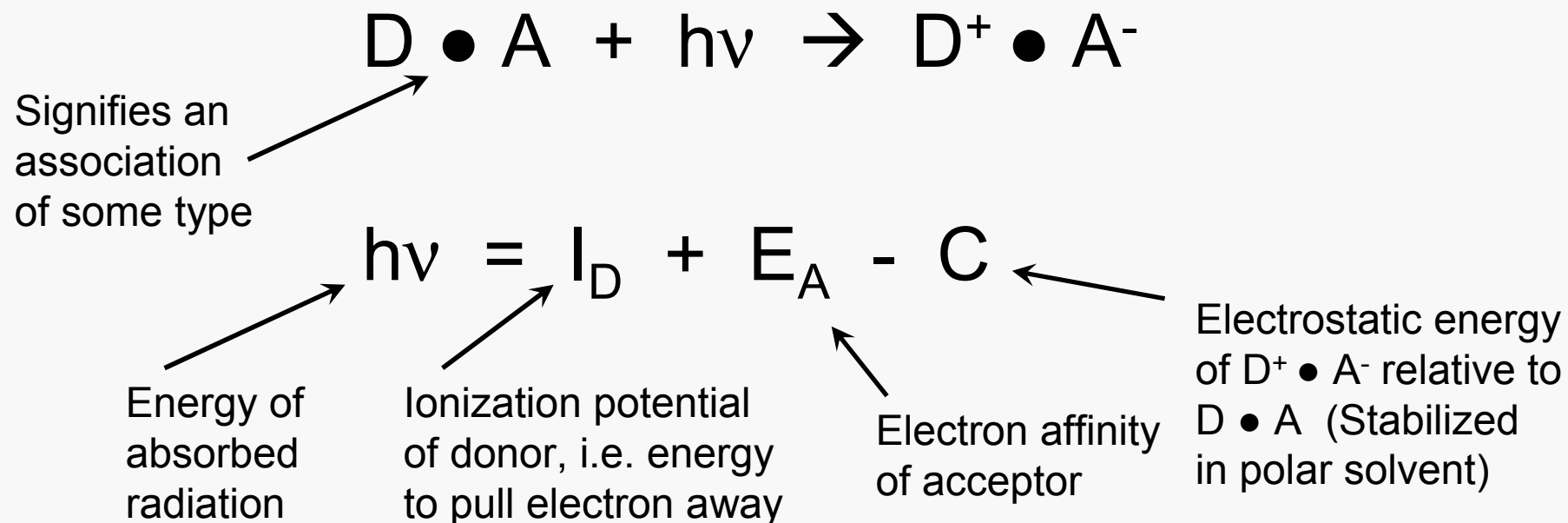
Intramolecular charge transfer

Charge transfer absorption usually has a value of $\varepsilon = 10^3 - 10^4$
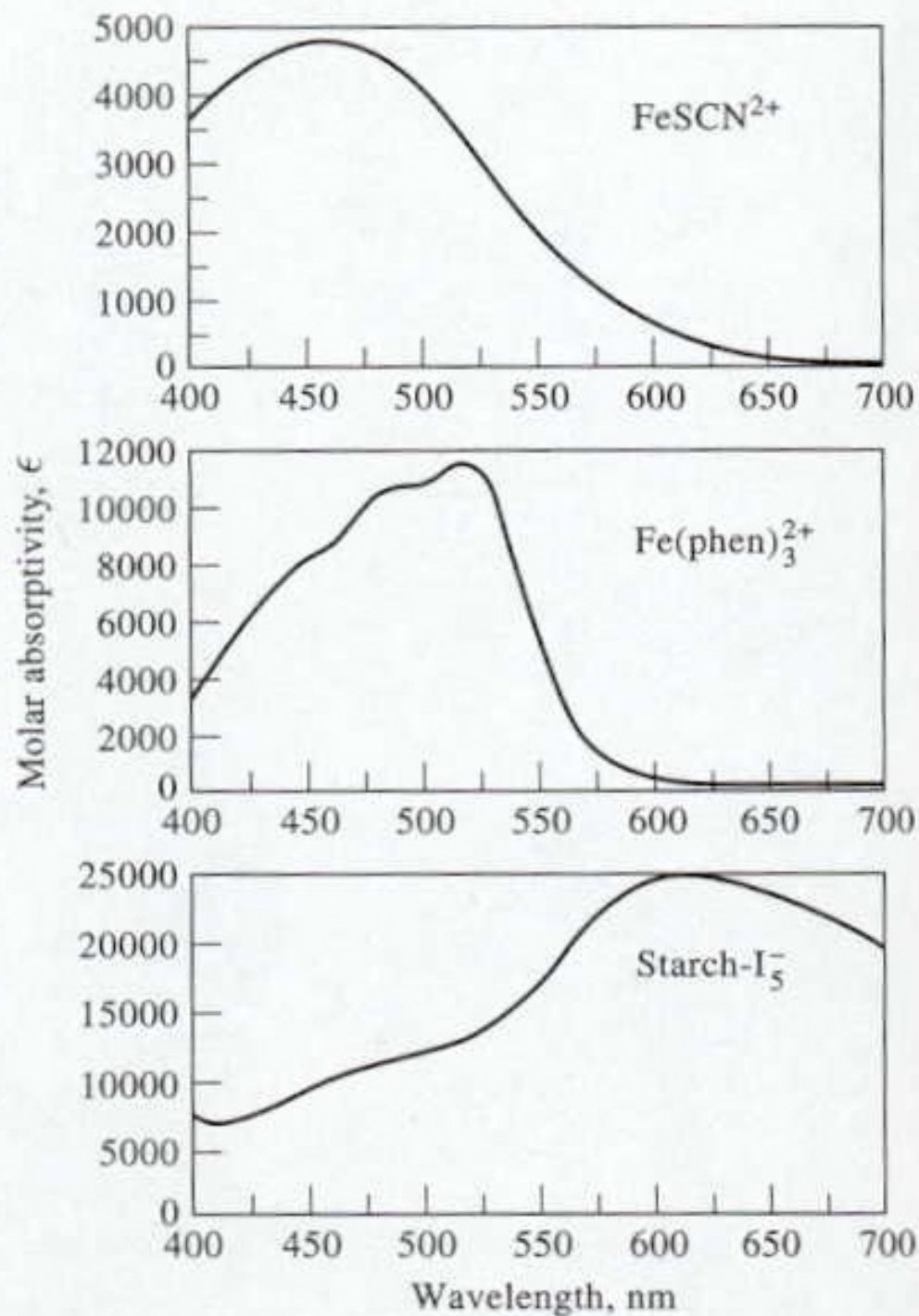
Charge-transfer spectra of 3 species

Note wavelengths are in a low energy region of the spectrum

Ligand-Field Absorption

When a transition metal dissolves in a solvent like water, it coordinates solvent molecules or other ligands which split the energies of the d orbitals. Water tends to give octahedral coordination, but other ligands may exhibit tetrahedral or square planer splitting.
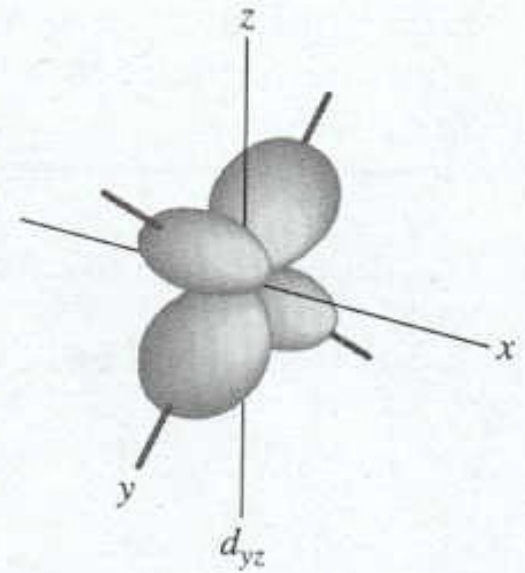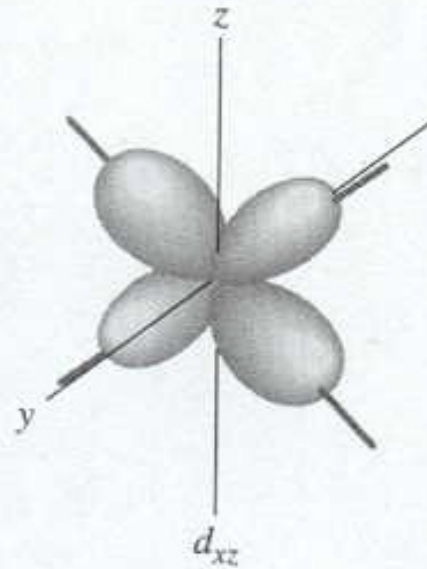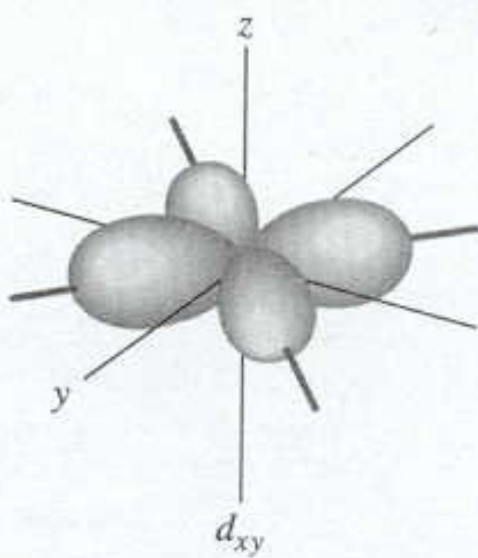
Ligand-field absorption involves an electron going from one d level to another, i.e. transition from lower d orbital to higher one.
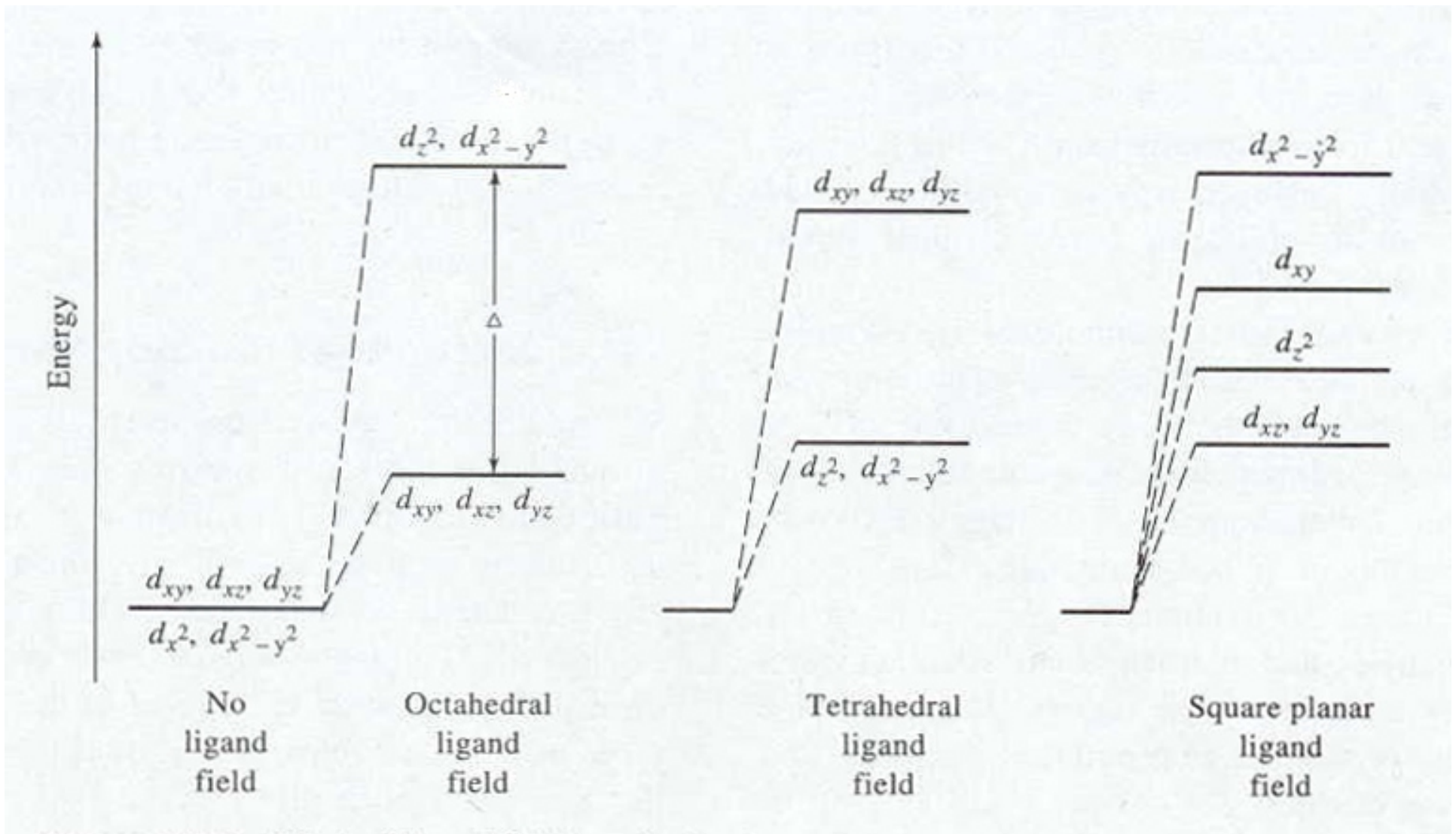
Ligand field splitting for three types of transition metal coordination complexes

Characteristics of ligand-field absorption:

1)   Low values for ε (10^{-1} – 10^2) because these transitions are forbidden

2)   Larger charge on the metal → more interaction → larger Δ → absorption at shorter λ

3)   Larger d orbitals (i.e. 4d relative to 3d) →closer to ligand → more interaction → larger Δ → absorption at shorter λ

4)   Nature of ligand affects Δ; usual order of increasing Δ → I^- < Br^- < Cl^- < F^- <OH^- < $C_2O_4^{2-}$ <$C_2H_5O^-$ < H_2O < SCN^- = NH_3 = en = NO_2^- = 1,10 phenanthroline = CN^- = CO

d_{xy} d_{xz} d_{yz} d_{z^2} $d_{z^2-y^2}$

Electron density distribution in the five d orbitals

Characteristics of ligand-field absorption:

1) Low values for ε ($10^{-1} - 10^2$) because these transitions are forbidden

2) Larger charge on the metal $\rightarrow$ more interaction $\rightarrow$ larger Δ $\rightarrow$ absorption at shorter λ

3) Larger d orbitals (i.e. 4d relative to 3d) $\rightarrow$ closer to ligand $\rightarrow$ more interaction $\rightarrow$ larger Δ $\rightarrow$ absorption at shorter λ

4) Nature of ligand affects Δ; usual order of increasing Δ $\rightarrow$ $I^- <$ $Br^- < Cl^- < F^- < OH^- <$ $C_2O_4^{2-} < C_2H_5O^- < H_2O < SCN^- = NH_3 = en = NO_2^- = 1,10$ phenanthroline $= CN^- = CO$

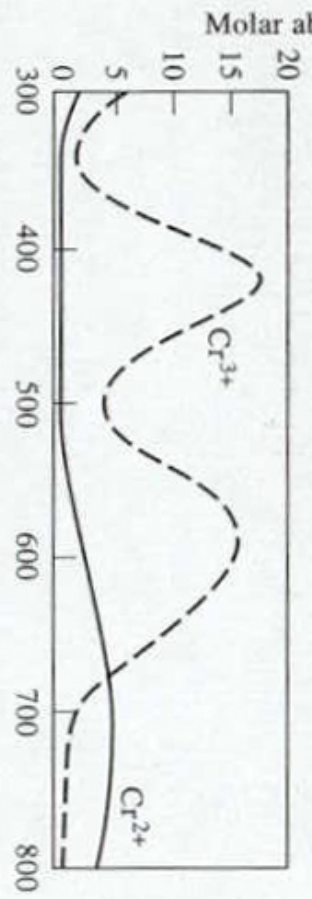# Effect of Ligands on Absorption Maxima Associated with d → d Transitions

Central Ion	λ_{max}(nm) for the Indicated Ligands				
	Increasing Ligand Field Strength→				
	6Cl$^-$	6H$_2$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	—

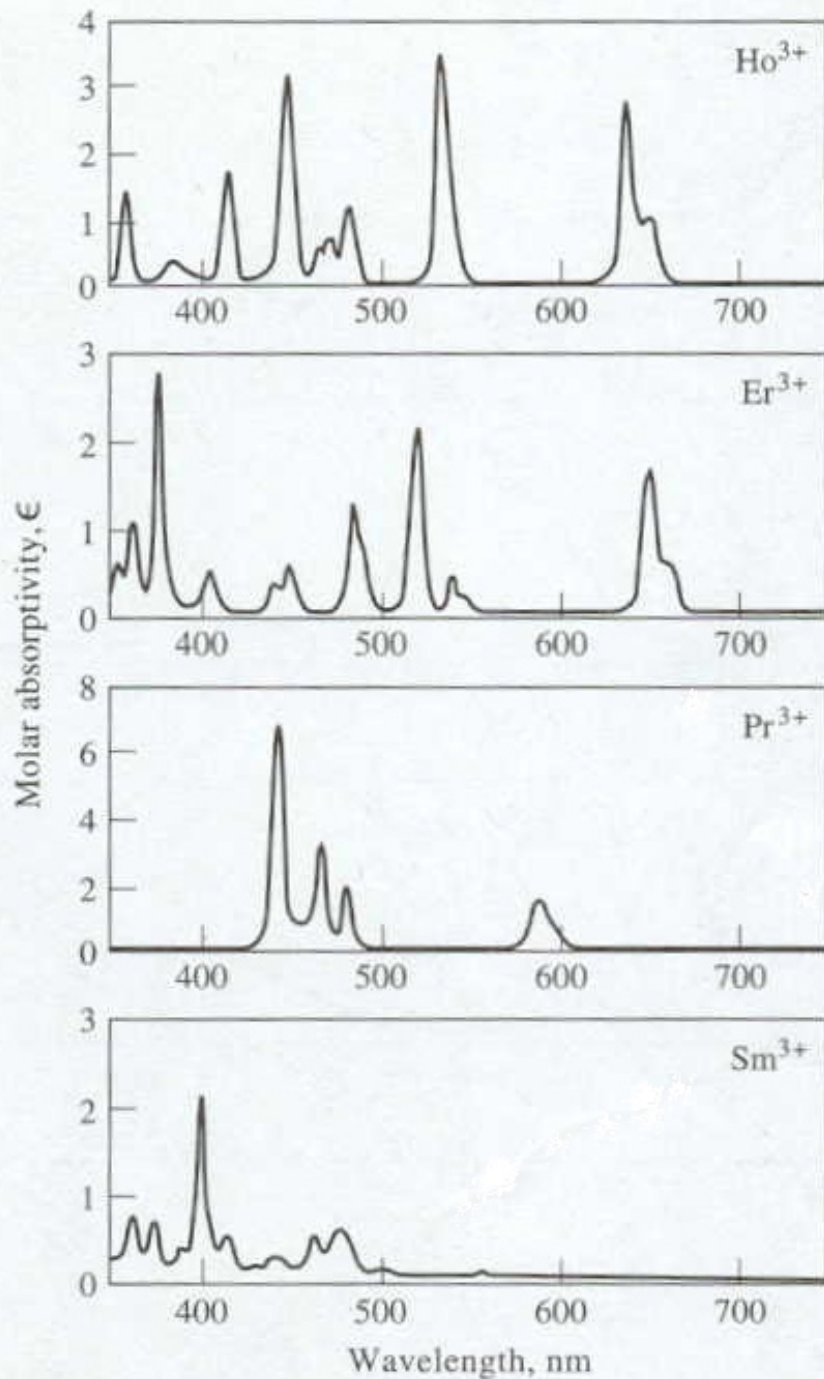Characteristics of ligand-field absorption:

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Effect of Ligands on Absorption Maxima Associated with d → d Transitions

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Molar absorptivity, ϵ

Wavelength, nm

Ti^{3+}

V^{3+}

Cr^{3+}

Cr^{2+}

Mn^{2+}

Fe^{2+}

Co^{2+}

Ni^{2+}

Cu^{2+}

Spectra for some lanthanide ions in solution

Peaks correspond to the energy of transitions between f orbitals

Narrow peaks