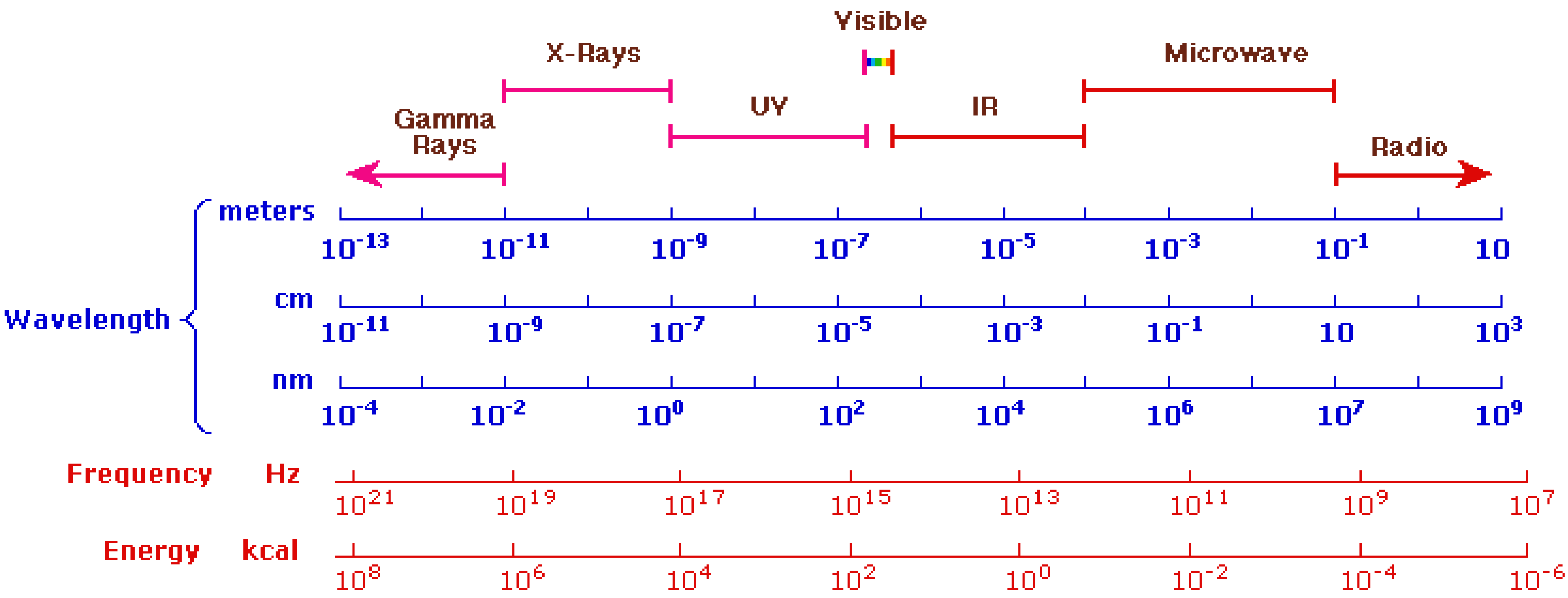
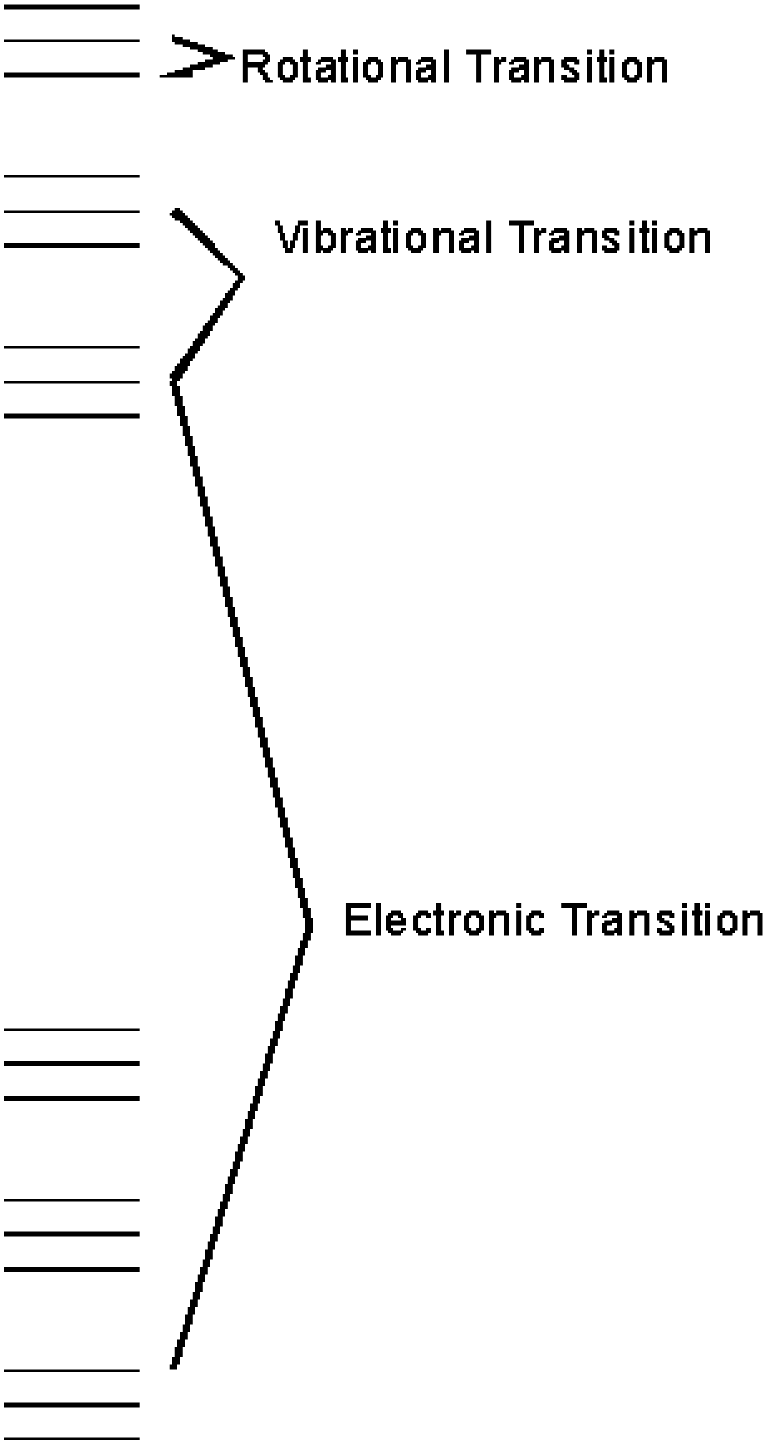
Chemistry 4631

Instrumental Analysis

Lecture 5

The Electromagnetic Spectrum





Rotational Transition

Vibrational Transition

Electronic Transition

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:

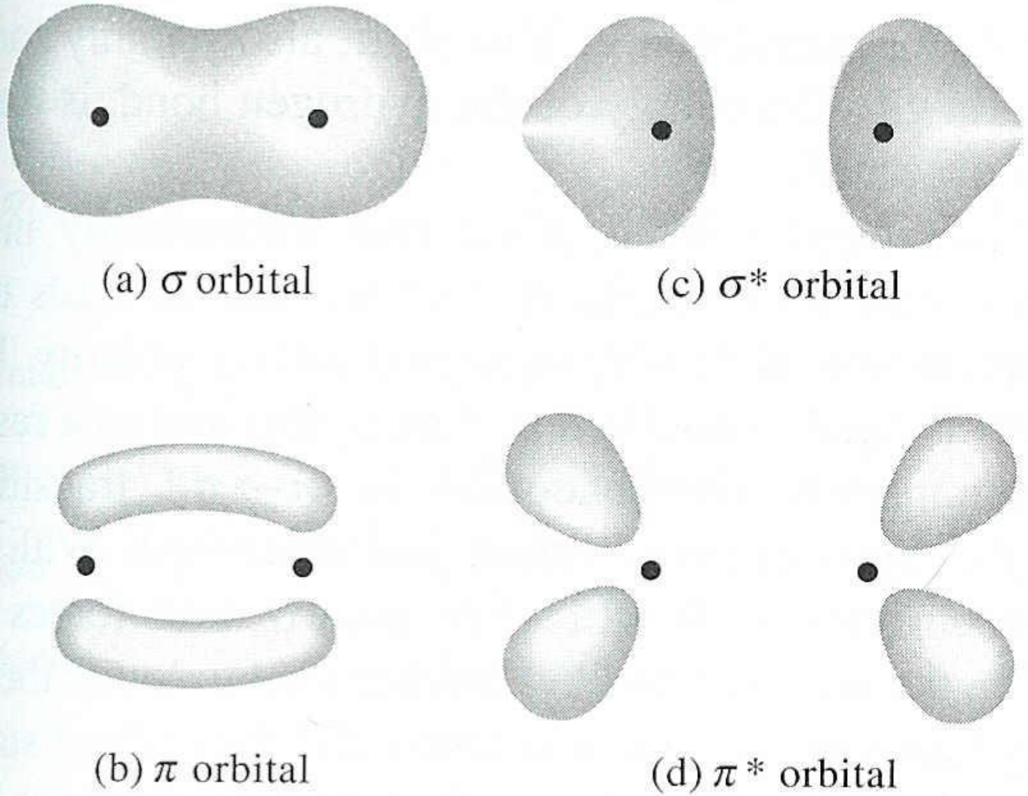
- Low energy bonding molecular orbital
- High energy antibonding molecular orbital

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

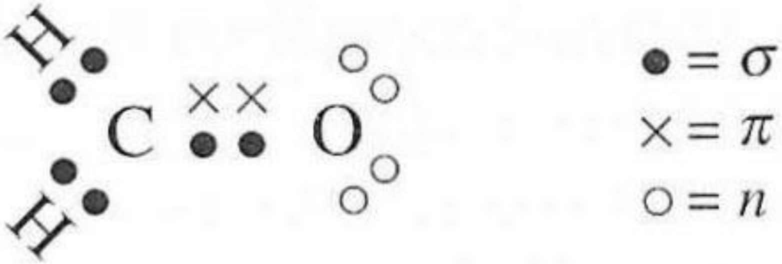


Figure 14-2 Types of molecular orbitals in formaldehyde.

Theory for UV/vis Spectrometry

Electronic transitions are designated as

- $\sigma \rightarrow \sigma^*$
- $n \rightarrow \sigma^*$
- $n \rightarrow \pi^*$
- $\pi \rightarrow \pi^*$

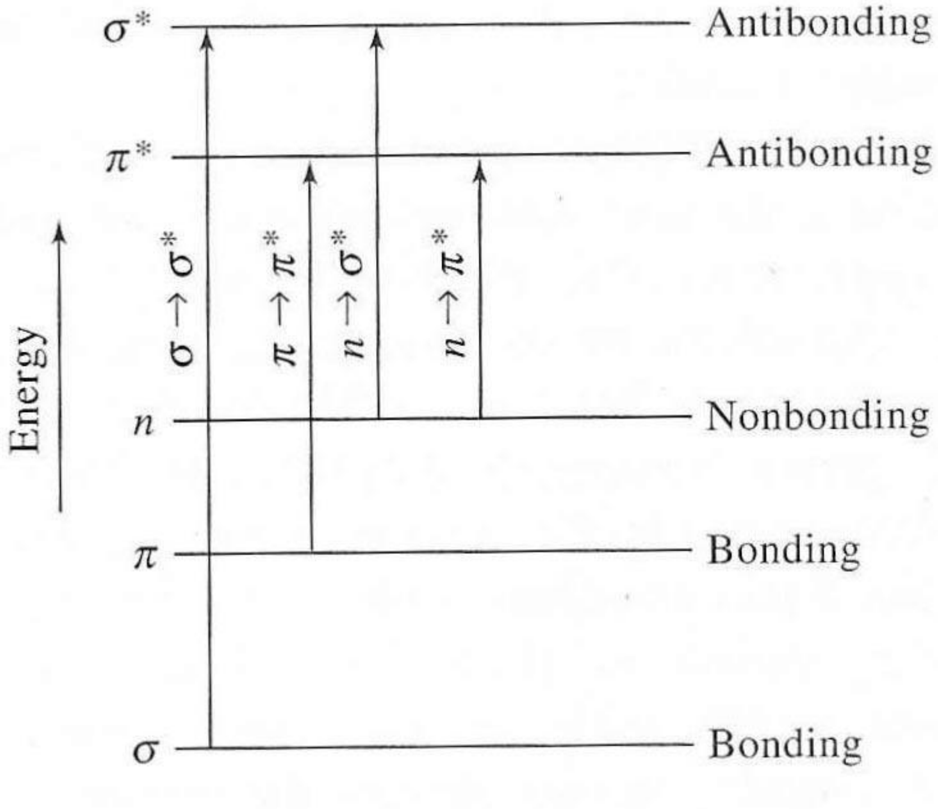


Figure 14-3 Electronic molecular energy levels.

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 → σ* Transitions

Occur in compounds containing atoms with unshared electrons.

Absorption region 150 to 250 nm

Theory for UV/vis Spectrometry

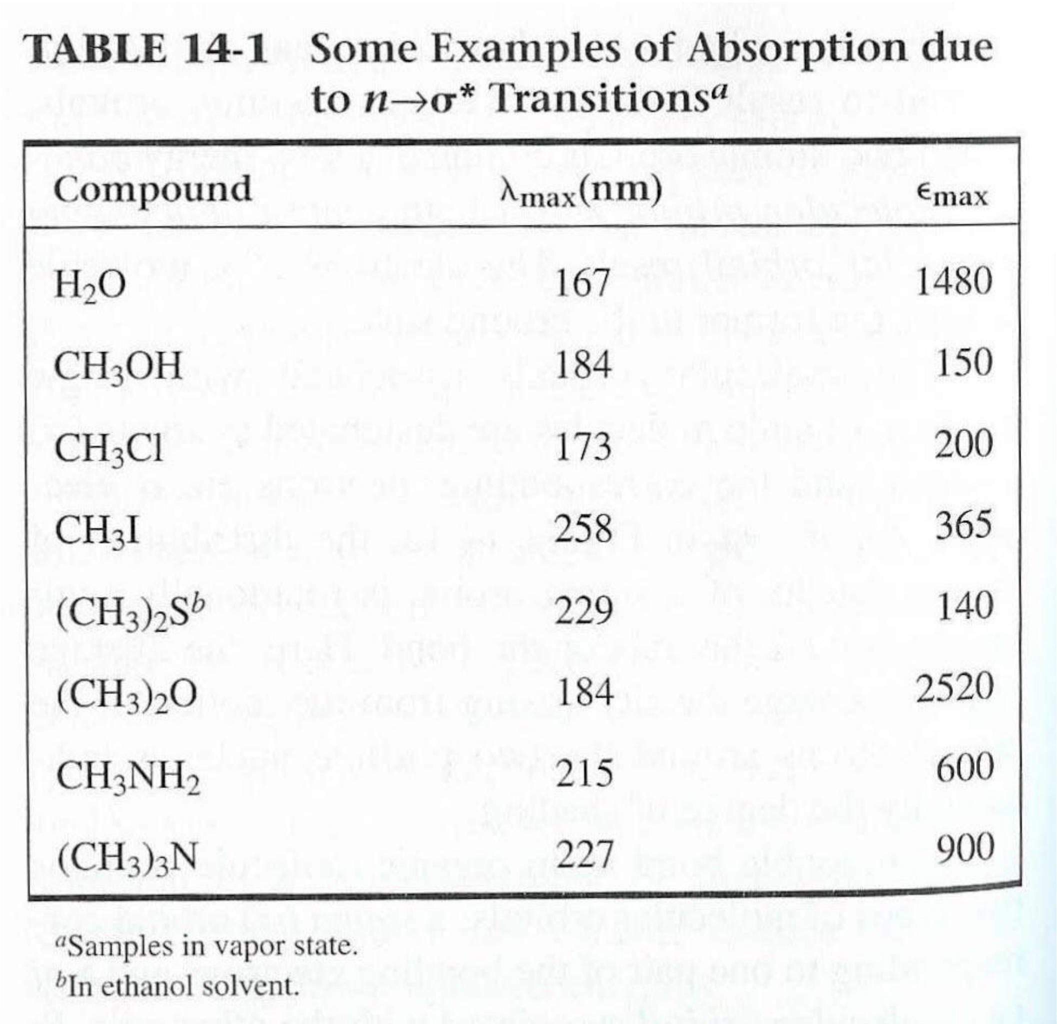


TABLE 14-1 Some Examples of Absorption due to $n \rightarrow \sigma^*$ Transitions[a]

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 → π* and π → π* Transitions

- Absorption region 200 – 700 nm
- Transition requires presence of unsaturated functional groups to provide π orbitals.

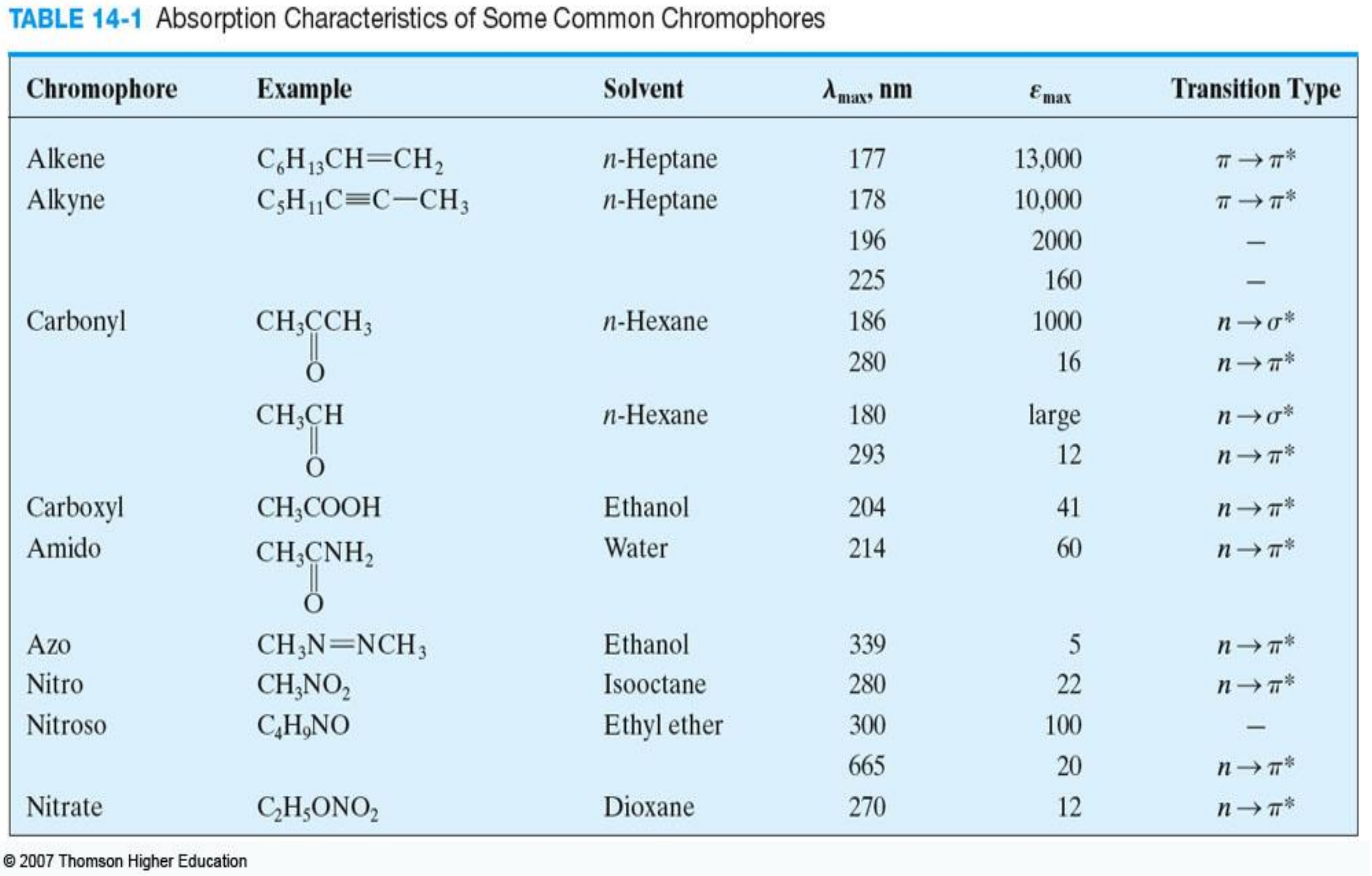


TABLE 14-1 Absorption Characteristics of Some Common Chromophores

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 – See Lab Lecture 2

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

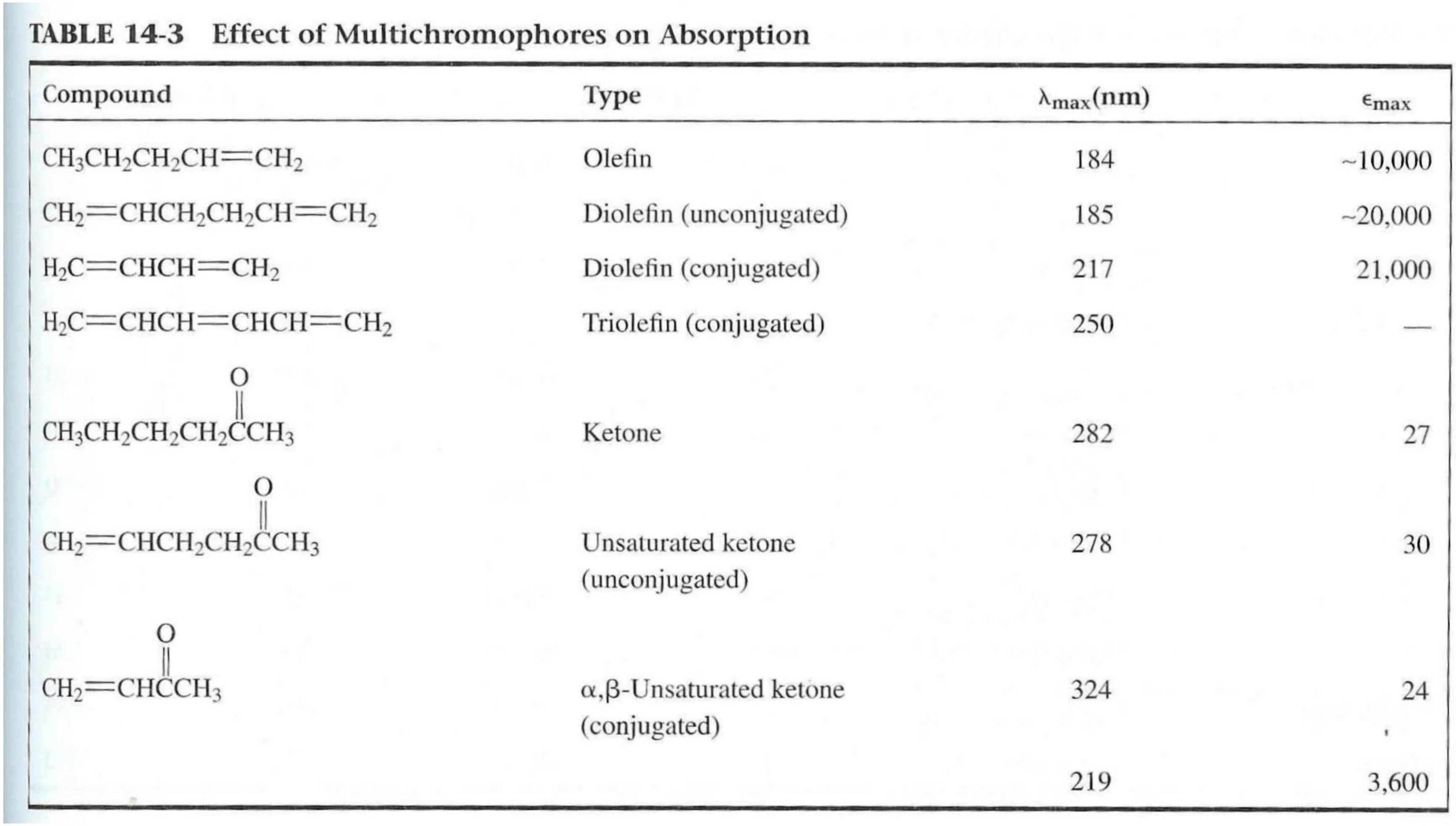


TABLE 14-3 Effect of Multichromophores on Absorption

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	—
$CH_3CH_2CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3$	Ketone	282	27
$CH_2{=}CHCH_2CH_2\overset{\overset{O}{\|}}{C}CH_3$	Unsaturated ketone (unconjugated)	278	30
$CH_2{=}CH\overset{\overset{O}{\|}}{C}CH_3$	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).

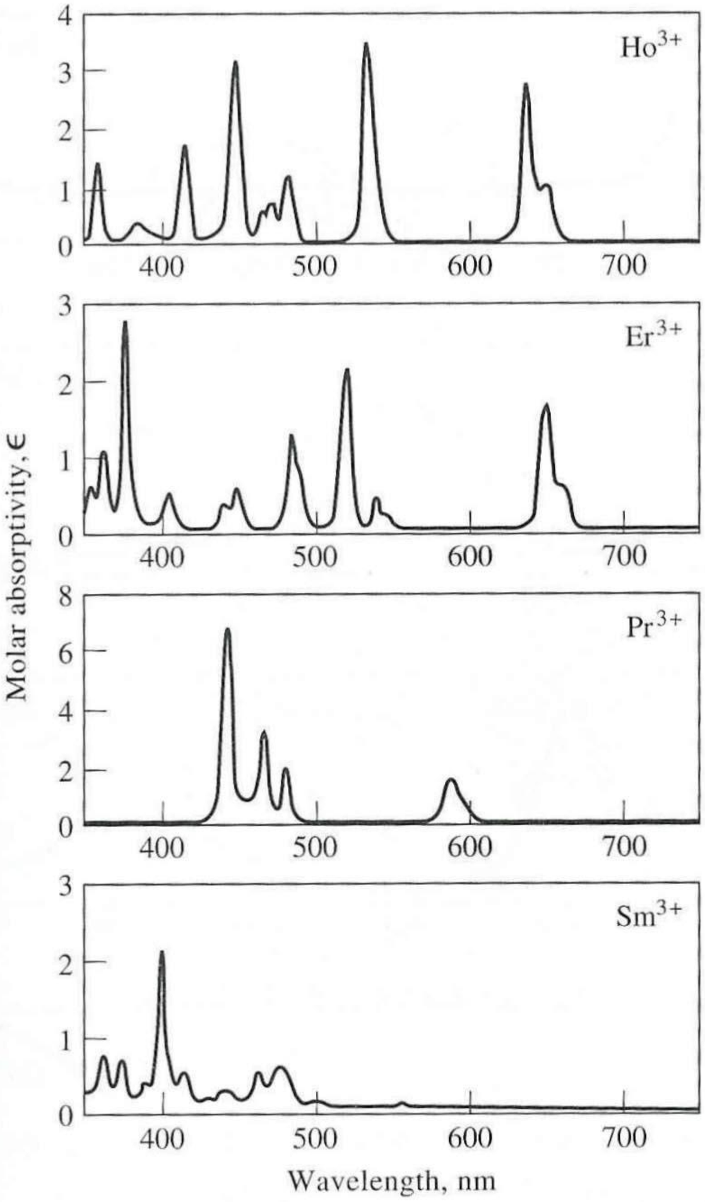


Figure 14-6 Typical absorption spectra for lanthanide ions.

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

See Lab Lecture 2

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

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

See Lab Lecture 2

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).

Fluorescence Spectroscopy

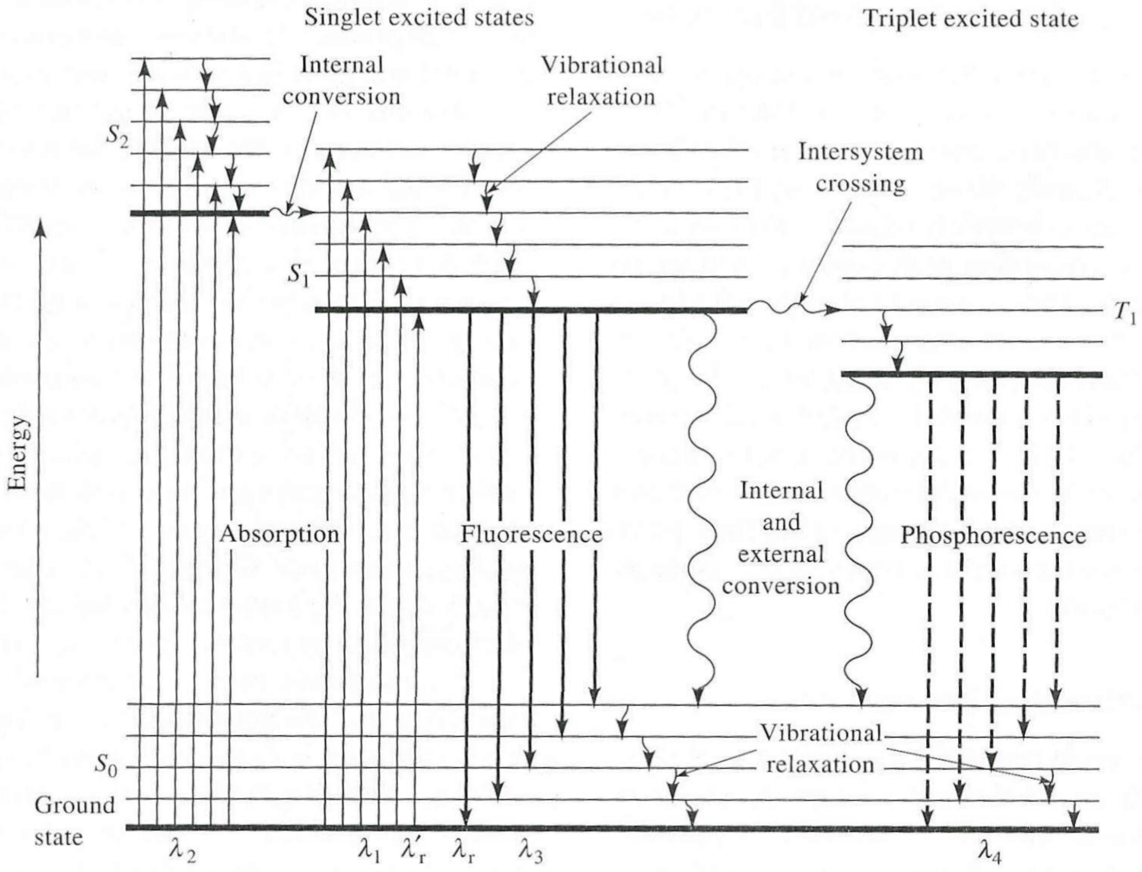


Figure 15-1 Partial energy diagram for a photoluminescent system.

Molecular Luminescence Spectrometry

Transition type

- Fluorescence seldom seen for λ's lower than 250 nm, because at these λ's predissociation or dissociation occurs.
- Seldom see $\sigma^* \rightarrow \sigma$ transitions for fluorescence
- Fluorescence due to $\pi^* \rightarrow \pi$ and $\pi^* \rightarrow n$ processes

Molecular Luminescence Spectrometry

Structure

Fluorescence more common in compounds having aromatic functional groups with low energy $\pi \rightarrow \pi^*$ transition levels.

Molecular Luminescence Spectrometry

Structure

Fluorescence higher with increasing number of rings.

Molecular Luminescence Spectrometry

Substitution on the rings also affect fluorescence:

Groups with non-bonding electrons enhance fluorescence

-NH_2, -OH, -F, -OCH_3, -NHR and –NR_2

Groups with electron withdrawing groups quench fluorescence

-COOH, -NO_2, -NH-CO-CH_3, -Cl, -Br, -I

Molecular Luminescence Spectrometry

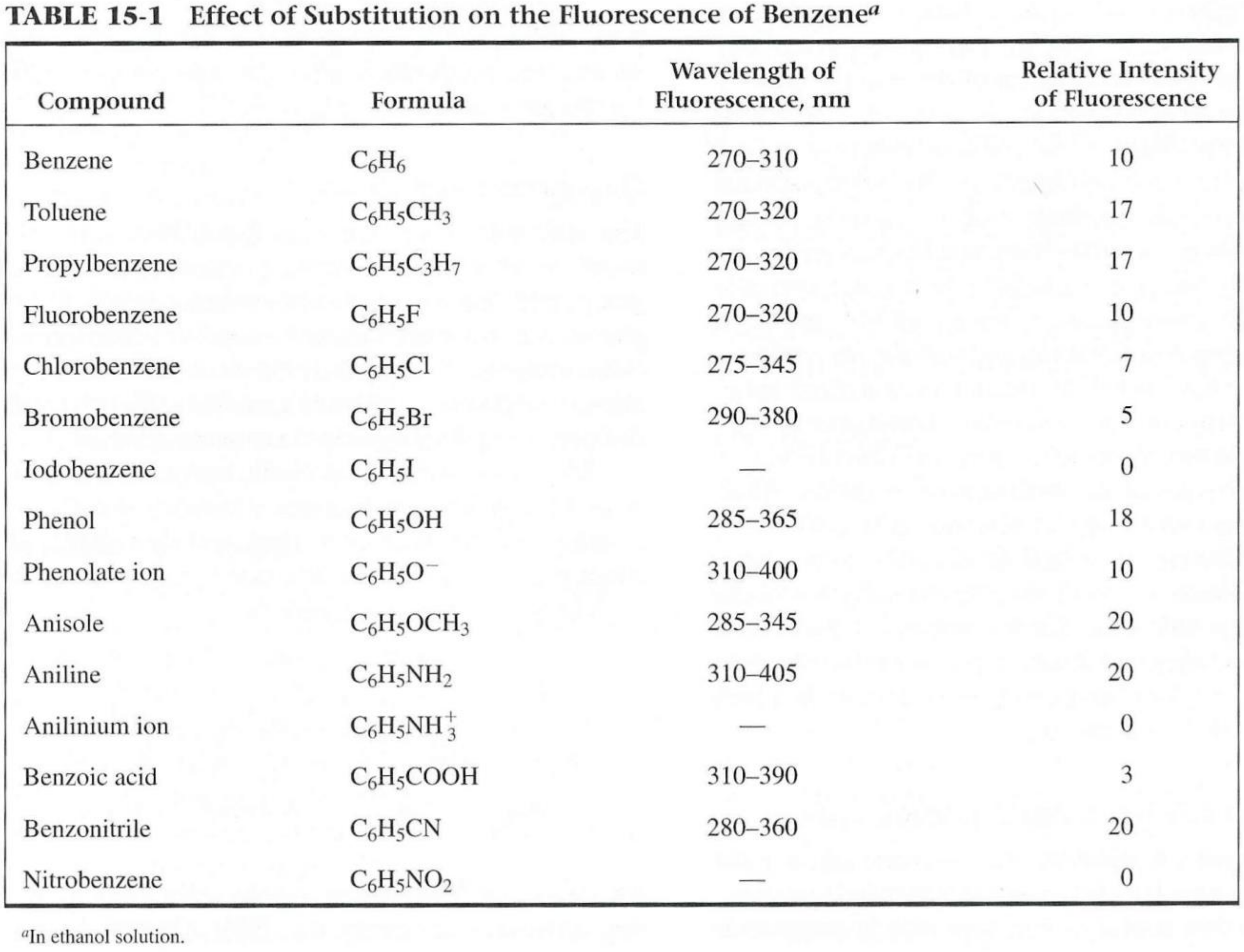


TABLE 15-1 Effect of Substitution on the Fluorescence of Benzene[a]

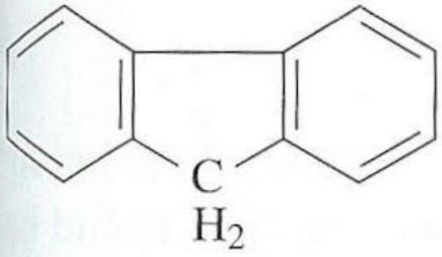
Compound	Formula	Wavelength of Fluorescence, nm	Relative Intensity of Fluorescence
Benzene	C_6H_6	270–310	10
Toluene	$C_6H_5CH_3$	270–320	17
Propylbenzene	$C_6H_5C_3H_7$	270–320	17
Fluorobenzene	C_6H_5F	270–320	10
Chlorobenzene	C_6H_5Cl	275–345	7
Bromobenzene	C_6H_5Br	290–380	5
Iodobenzene	C_6H_5I	—	0
Phenol	C_6H_5OH	285–365	18
Phenolate ion	$C_6H_5O^-$	310–400	10
Anisole	$C_6H_5OCH_3$	285–345	20
Aniline	$C_6H_5NH_2$	310–405	20
Anilinium ion	$C_6H_5NH_3^+$	—	0
Benzoic acid	C_6H_5COOH	310–390	3
Benzonitrile	C_6H_5CN	280–360	20
Nitrobenzene	$C_6H_5NO_2$	—	0

[a] In ethanol solution.

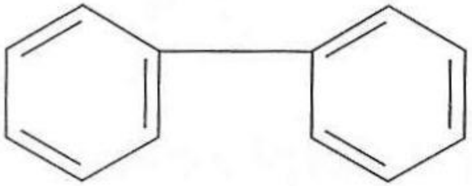
Molecular Luminescence Spectrometry

Effects on Fluorescence

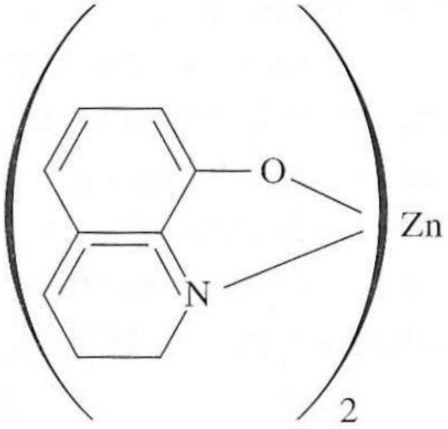
- Very rigid structures are more likely to fluorescence.
- Complexing will increase fluorescence.



fluorene



biphenyl



Molecular Luminescence Spectrometry

Effects on Fluorescence

- Fluorescence decreases with increasing temperature – more collisions.

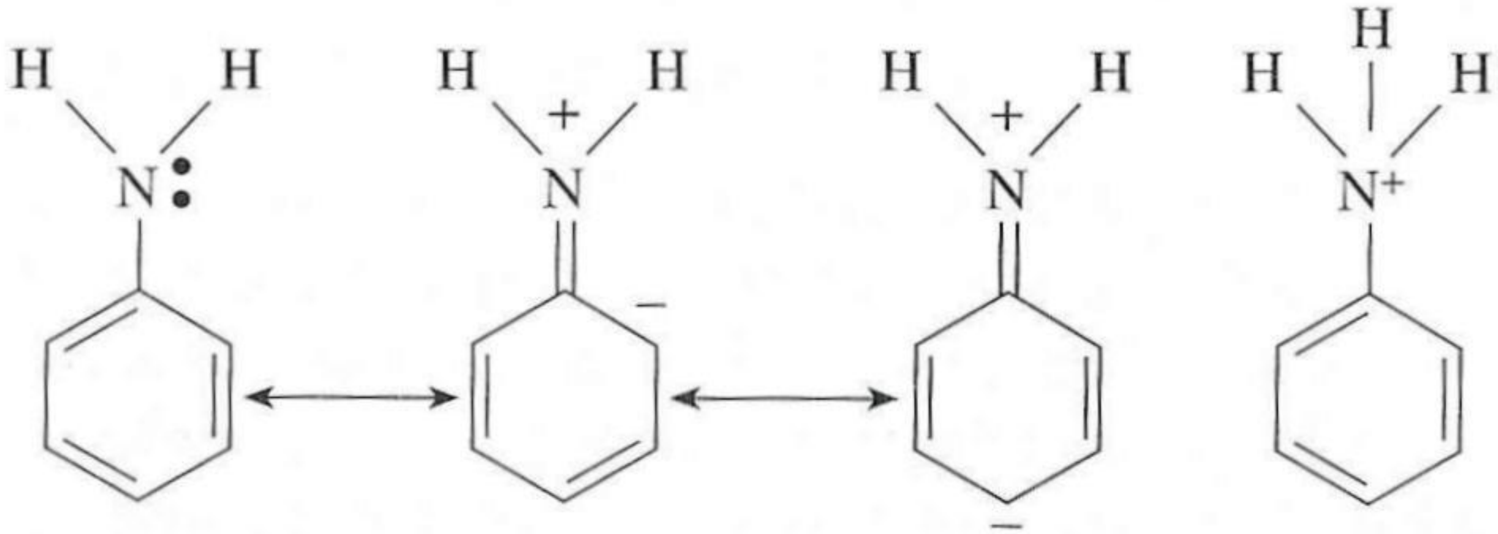
- Fluorescence decreases with solvents containing heavy atoms, (increases rate of triplet formation).

- Fluorescence decreases with dissolved oxygen (has paramagnetic properties, promotes intersystem crossing to triplet state).

Molecular Luminescence Spectrometry

Effects on Fluorescence

- Fluorescence increases with more resonance forms



resonance forms of aniline

anilinium ion

Molecular Luminescence Spectrometry

Quantum yield –

# of fluorescence photons / # of absorbed photons (or # of excited molecules)

Molecular Luminescence Spectrometry

Quantitative Analysis using Fluorescence

$$F = I_o \ \phi_F \ f(\theta) \ g(\lambda) \ (1 - e^{-\varepsilon bc})$$

ϕ_F - quantum efficiency

$f(\theta)$ - geometric factor (usually 90^o)

$g(\lambda)$ - efficiency of detector as function of wavelength

Molecular Luminescence Spectrometry

Quantitative Analysis using Fluorescence

When $e^{-\varepsilon bc} < 0.5$ then

$$F = 2.3\, I_o\ \phi_F\ f(\theta)\ g(\lambda)\ e^{-\varepsilon bc}$$

Molecular Luminescence Spectrometry

Applications

Fluorescence and phosphorescence methods more sensitive than absorbance methods since Intensity is measured independently of the source, P_o.

However precision and accuracy are 2-5 times less than for absorbance methods.

Molecular Luminescence Spectrometry

Applications

Determination of Inorganic Species

Non-transition metal ions form fluorescing chelates over transition metals because transition metals tend to be paramagnetic and deactivation is more likely by internal conversion.

Molecular Luminescence Spectrometry

Fluorometric Reagents

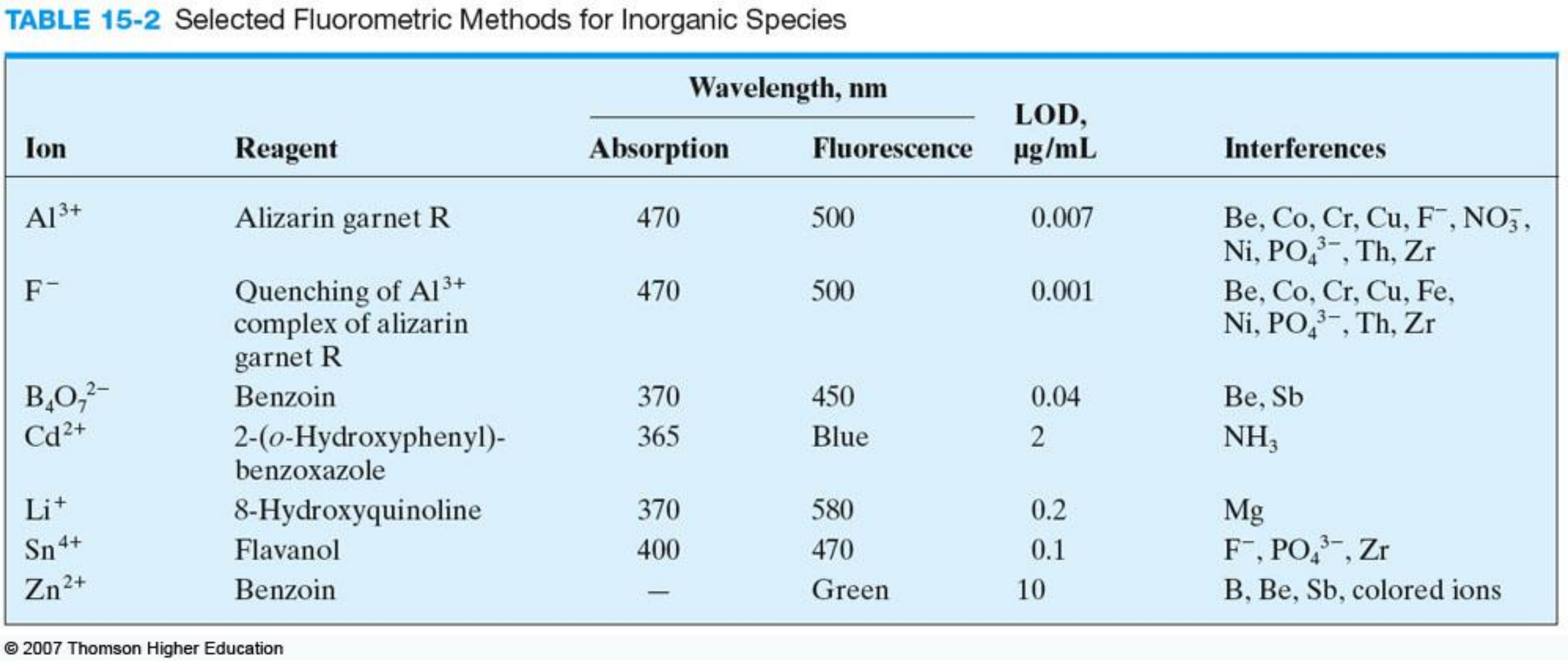


TABLE 15-2 Selected Fluorometric Methods for Inorganic Species

Ion	Reagent	Wavelength, nm Absorption	Wavelength, nm Fluorescence	LOD, µg/mL	Interferences
Al^{3+}	Alizarin garnet R	470	500	0.007	Be, Co, Cr, Cu, F^-, NO_3^-, Ni, PO_4^{3-}, Th, Zr
F^-	Quenching of Al^{3+} complex of alizarin garnet R	470	500	0.001	Be, Co, Cr, Cu, Fe, Ni, PO_4^{3-}, Th, Zr
$B_4O_7^{2-}$	Benzoin	370	450	0.04	Be, Sb
Cd^{2+}	2-(*o*-Hydroxyphenyl)-benzoxazole	365	Blue	2	NH_3
Li^+	8-Hydroxyquinoline	370	580	0.2	Mg
Sn^{4+}	Flavanol	400	470	0.1	F^-, PO_4^{3-}, Zr
Zn^{2+}	Benzoin	—	Green	10	B, Be, Sb, colored ions

Molecular Luminescence Spectrometry

Applications

Determination of organic species

Used for enzymes, coenzymes, medical agents, plant products, steroids, vitamins, food products and more.

Widely used technique for a vast range of organics.

Molecular Luminescence Spectrometry

Applications

Lifetime Measurements

To study luminescence decay rates need mode-lock lasers to produce pulses of radiation with widths of 70-100 ps for excitation and fast-rise time PMTs for detection.

Molecular Luminescence Spectrometry

Applications

Lifetime Measurements

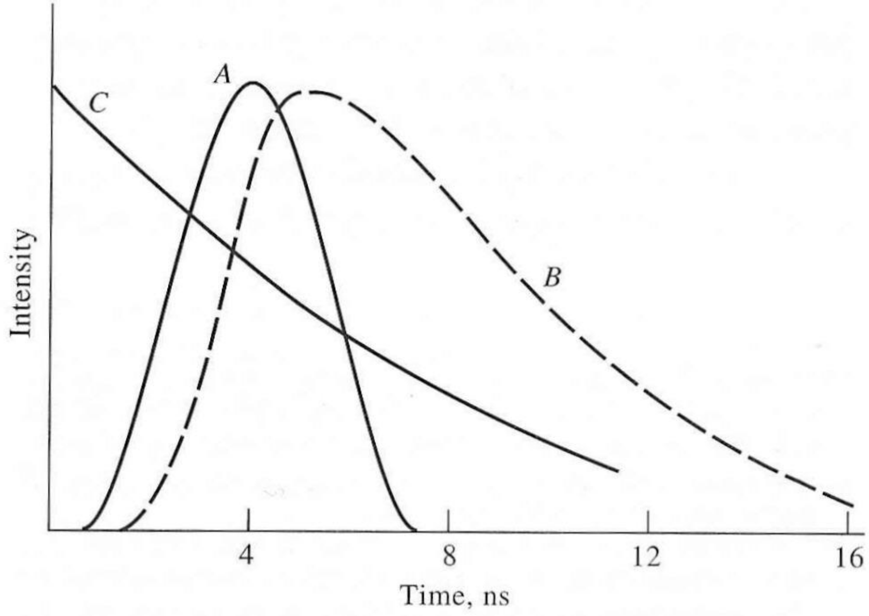


Figure 15-10 Fluorescence lifetime profiles: *A*, excitation pulse; *B*, measured decay curve; *C*, corrected decay curve.

Molecular Luminescence Spectrometry

Analysis of Gases

Used for determining atmospheric pollutants, i.e. ozone, nitrogen oxides, sulfurs.

Example. Determination of nitrogen monoxide

$$NO + O_3 \rightarrow NO_2^* + O_2$$

$$NO_2^* \rightarrow NO_2 + h\nu \ (\lambda = 600\text{-}2800 \text{ nm})$$

Molecular Luminescence Spectrometry

Analysis of Gases

Used for determining atmospheric pollutants, i.e. ozone, nitrogen oxides, sulfurs.

Example. Determination of atmospheric sulfur compounds

$$4H_2 + 2SO_2 \leftarrow\rightarrow S_2{}^* + 4H_2O$$

$$S_2{}^* \rightarrow S_2 + hv\ (\lambda = 384 \text{ and } 394 \text{ nm})$$

Assignment

- Read Chapter 6
- HW2: Ch. 6: 2-12, 14, 15, 18, 19 (extra credit) (Due 1-29)
- Go over Lab Lecture 2
- Read Chapter 15
- Read Chapter 16 & 17
- HW 3: Ch. 16: 7, 8, 11 and Ch. 17: 2, 4, 5 (Due 1-31)
- HW4: Ch. 15: 1, 2, 4, 5, 9, 13 (Due 2-2)