

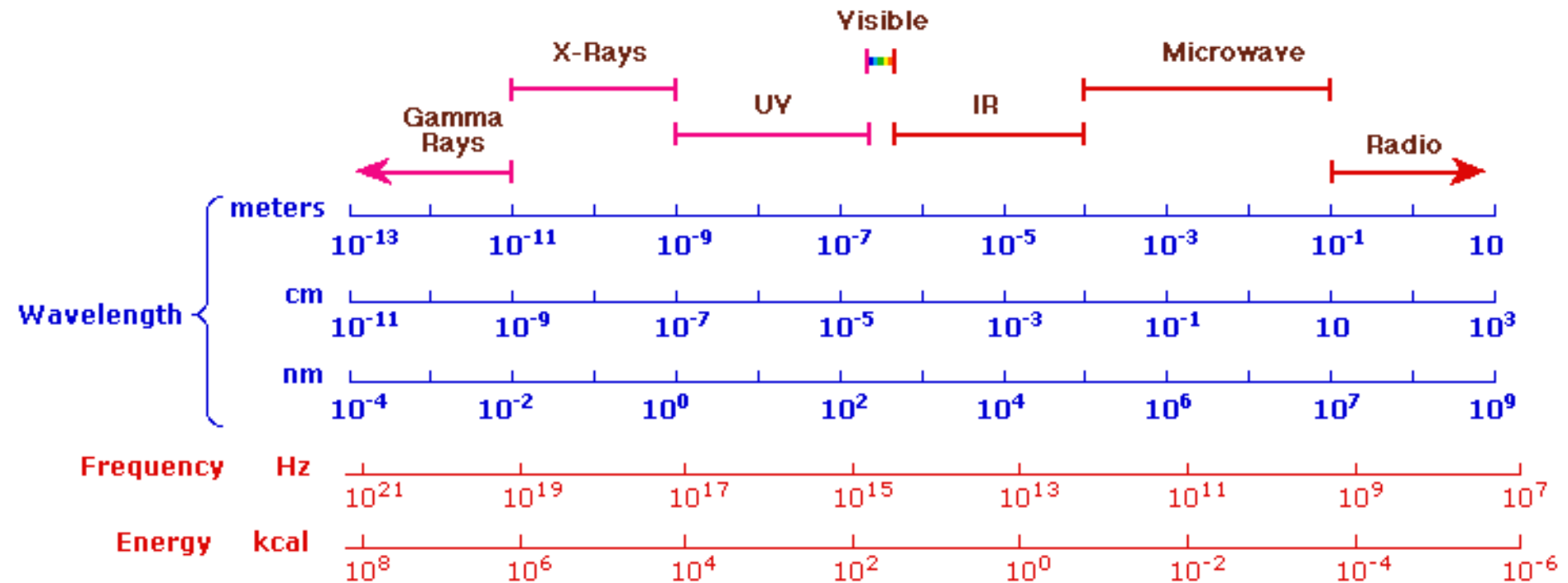


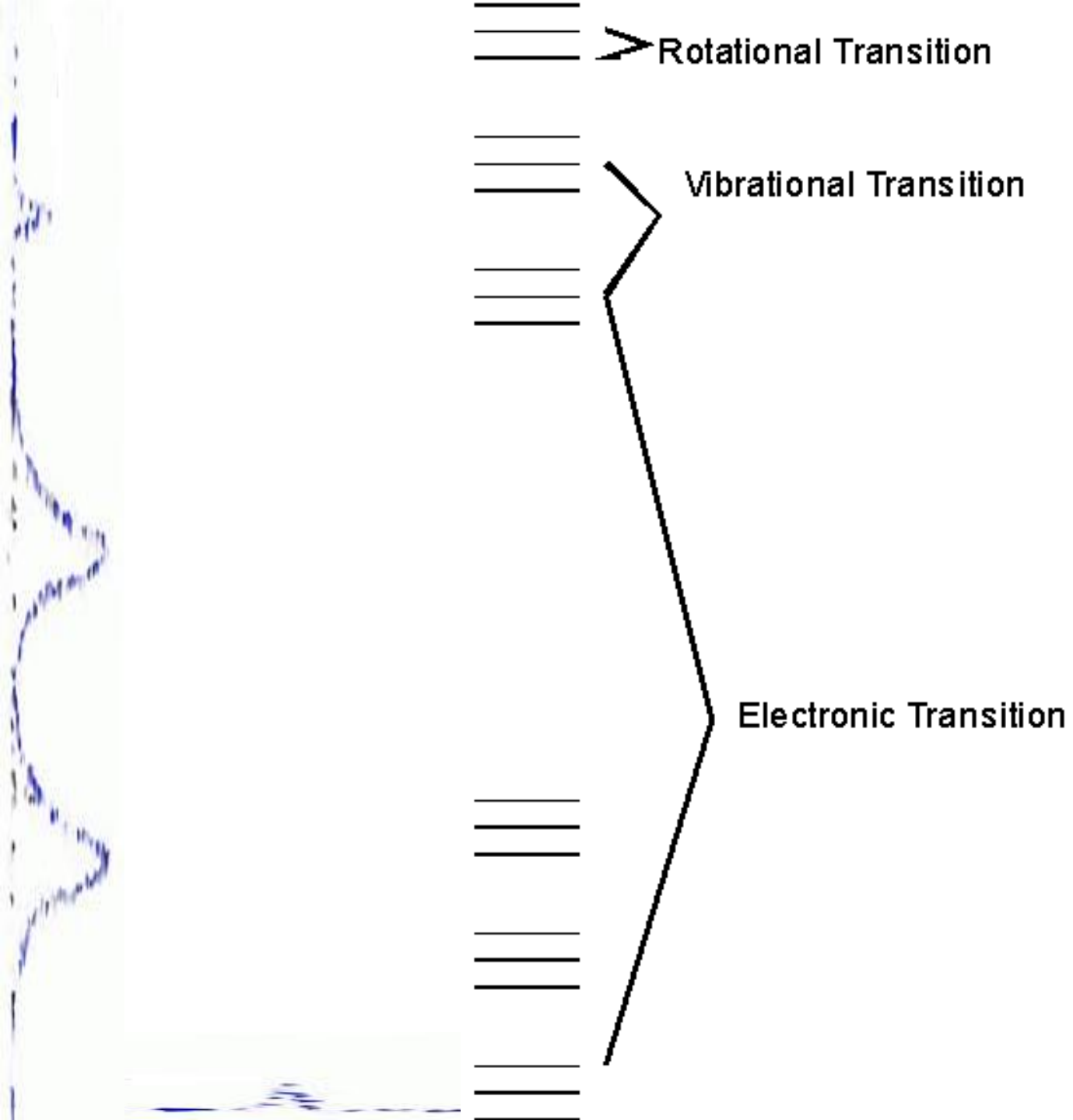
# Chemistry 4631

## Instrumental Analysis

### Lecture 4

## The Electromagnetic Spectrum





# Theory for UV/vis Spectrometry

## Molar Absorptivities

Range 0 to  $10^5$

Magnitude of  $\epsilon$  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,  $\text{cm}^2$

# Theory for UV/vis Spectrometry

## Molar Absorptivities

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

$P$  – transition probability

$A$  – cross-section target area,  $\text{cm}^2$

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.  $\lambda$  correlates to type of bond in species

Valuable in identifying functional groups

# Theory for UV/vis Spectrometry

## Absorbing Species

### Three types of electronic transitions:

- $\pi$ ,  $\sigma$ , and n electrons
- d and f electrons
- charge transfer electrons

# Theory for UV/vis Spectrometry

**Absorbing Species that contain  $\pi$ ,  $\sigma$ , 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:**

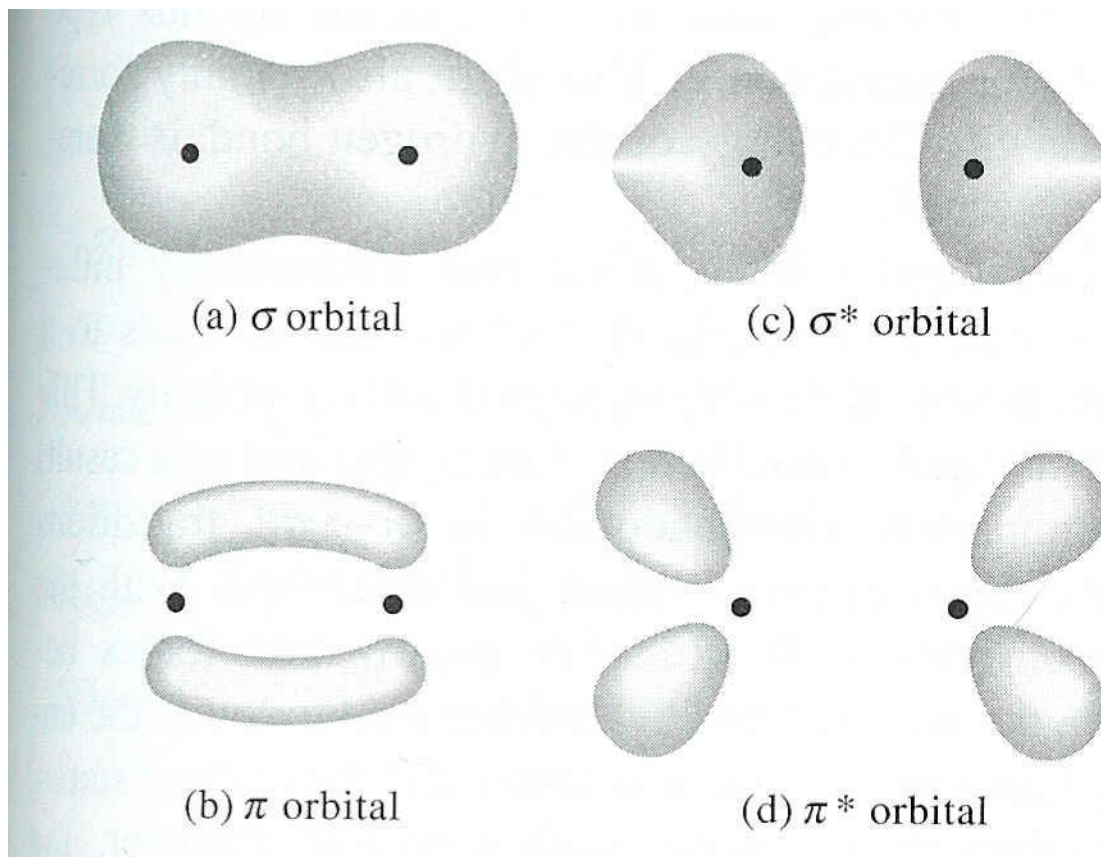
- Low energy bonding molecular orbital
- High energy antibonding molecular orbital

**Single bonds – sigma ( $\sigma$ ) orbitals**

**Double bonds – sigma ( $\sigma$ ) and pi ( $\pi$ ) orbitals**

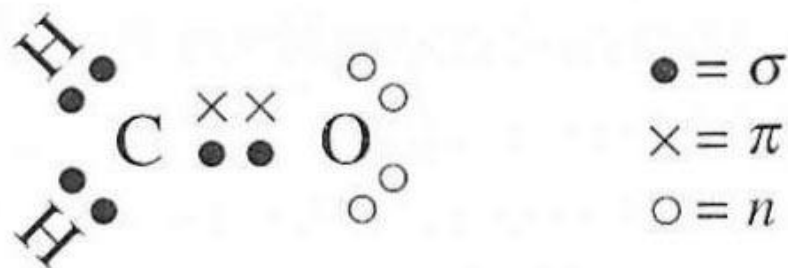
**Nonbonding electrons - n**

# 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

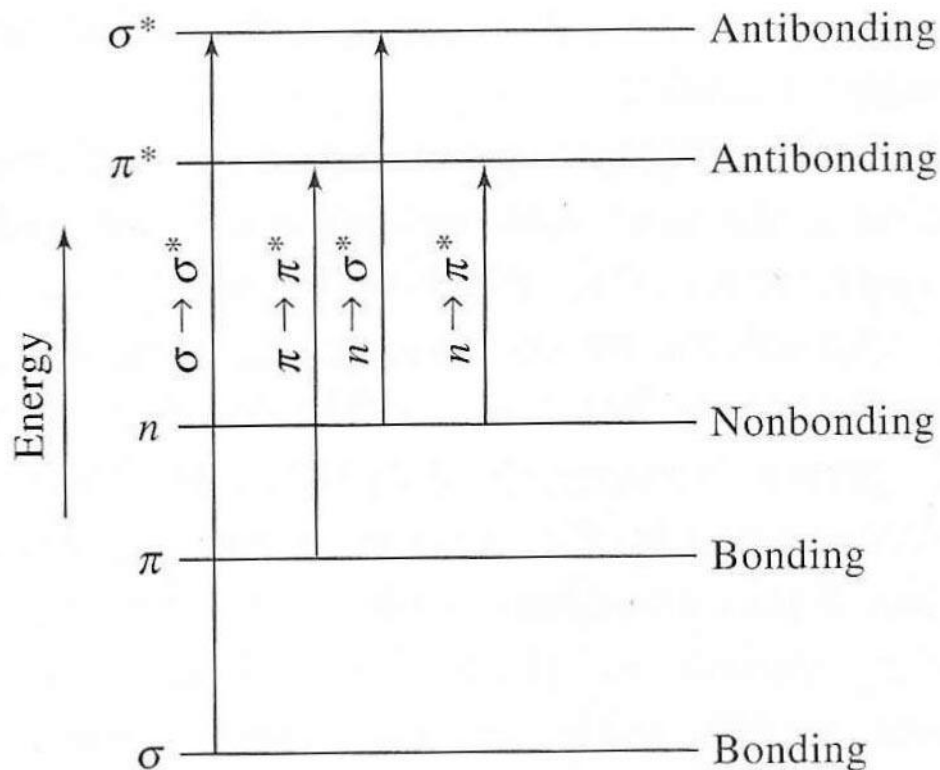


Figure 14-3 Electronic molecular energy levels.

# 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<sup>a</sup>

Compound	$\lambda_{\max}(\text{nm})$	$\epsilon_{\max}$
H <sub>2</sub> O	167	1480
CH <sub>3</sub> OH	184	150
CH <sub>3</sub> Cl	173	200
CH <sub>3</sub> I	258	365
(CH <sub>3</sub> ) <sub>2</sub> S <sup>b</sup>	229	140
(CH <sub>3</sub> ) <sub>2</sub> O	184	2520
CH <sub>3</sub> NH <sub>2</sub>	215	600
(CH <sub>3</sub> ) <sub>3</sub> N	227	900

<sup>a</sup>Samples in vapor state.

<sup>b</sup>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  $\pi$  orbitals.

**TABLE 14-1** Absorption Characteristics of Some Common Chromophores

Chromophore	Example	Solvent	$\lambda_{\max}$ , nm	$\epsilon_{\max}$	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 – See Lab Lecture 2

### Increasing polarity of the solvent:

- Shifts  $n \rightarrow \pi^*$  transitions to shorter  $\lambda$ 's (blue shift).
- Shifts  $\pi \rightarrow \pi^*$  Transitions to higher  $\lambda$ '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	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	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
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2=\text{CHCCH}_3 \end{array}$	$\alpha,\beta$ -Unsaturated ketone (conjugated)	324	24
		219	3,600

# Theory for UV/vis Spectrometry

## Absorbing Species

### Three types of electronic transitions:

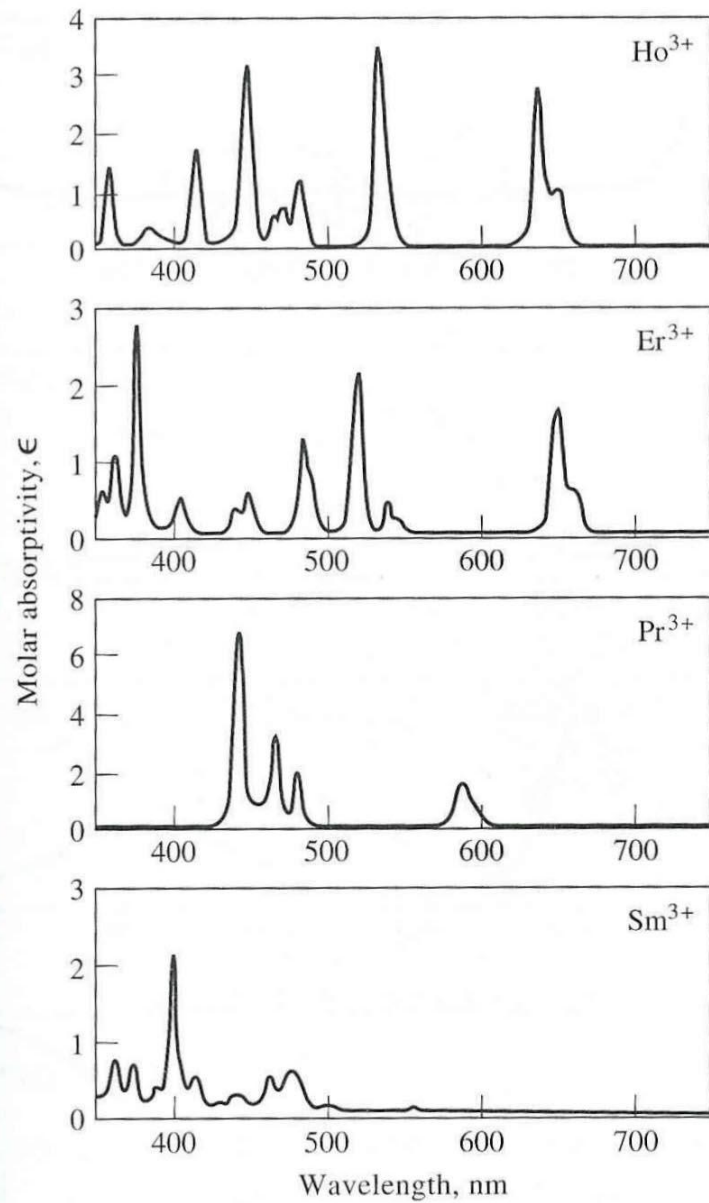
- $\pi$ ,  $\sigma$ , and n electrons
- d and f electrons**
- charge transfer electrons

# 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**

**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:

- $\pi$ ,  $\sigma$ , 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 ( $\epsilon_{\text{max}} > 10,000$ )**

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

# Atomic Spectroscopy

**TABLE 6-2** Major Classes of Spectrochemical Methods

<b>Class</b>	<b>Radiant Power Measured</b>	<b>Concentration Relationship</b>	<b>Type of Methods</b>
Emission	Emitted, $P_e$	$P_e = kc$	Atomic emission
Luminescence	Luminescent, $P_l$	$P_l = kc$	Atomic and molecular fluorescence, phosphorescence, and chemiluminescence
Scattering	Scattered, $P_{sc}$	$P_{sc} = kc$	Raman scattering, turbidimetry, and particle sizing
Absorption	Incident, $P_0$ , and transmitted, $P$	$-\log \frac{P}{P_0} = kc$	Atomic and molecular absorption

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# Components of Optical Instruments

**UV to IR**

**Optical spectroscopy are based on:**

- **absorption**
- **fluorescence**
- **phosphorescence**
- **scattering**
- **emission**
- **chemiluminescence**

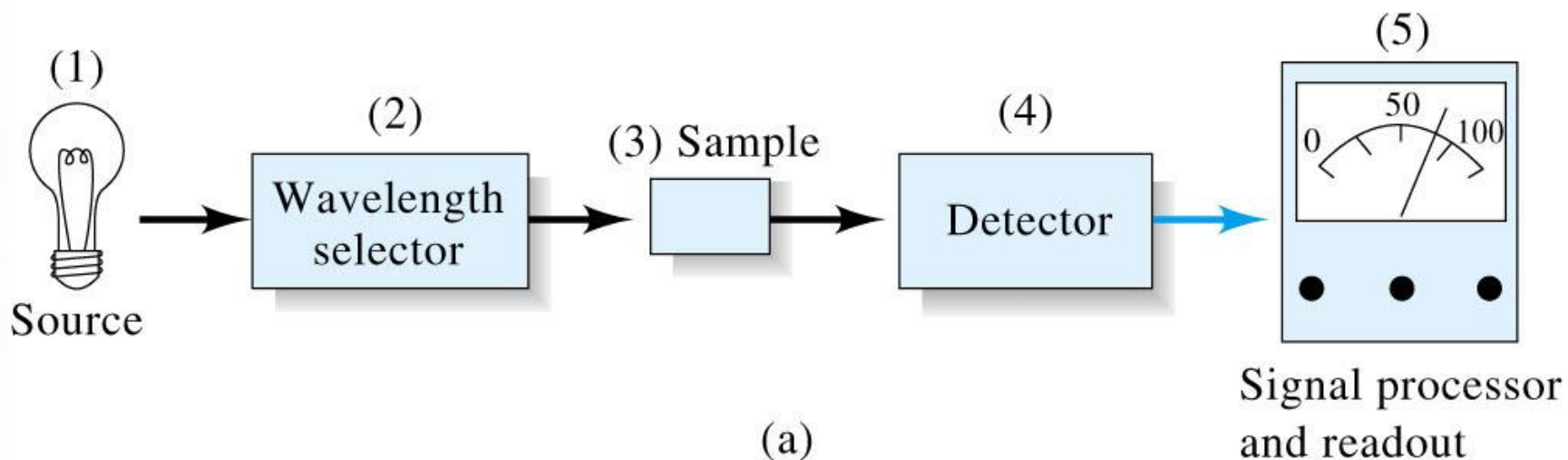
# Components of Optical Instruments

## UV to IR

### Basic components of spectroscopic instruments:

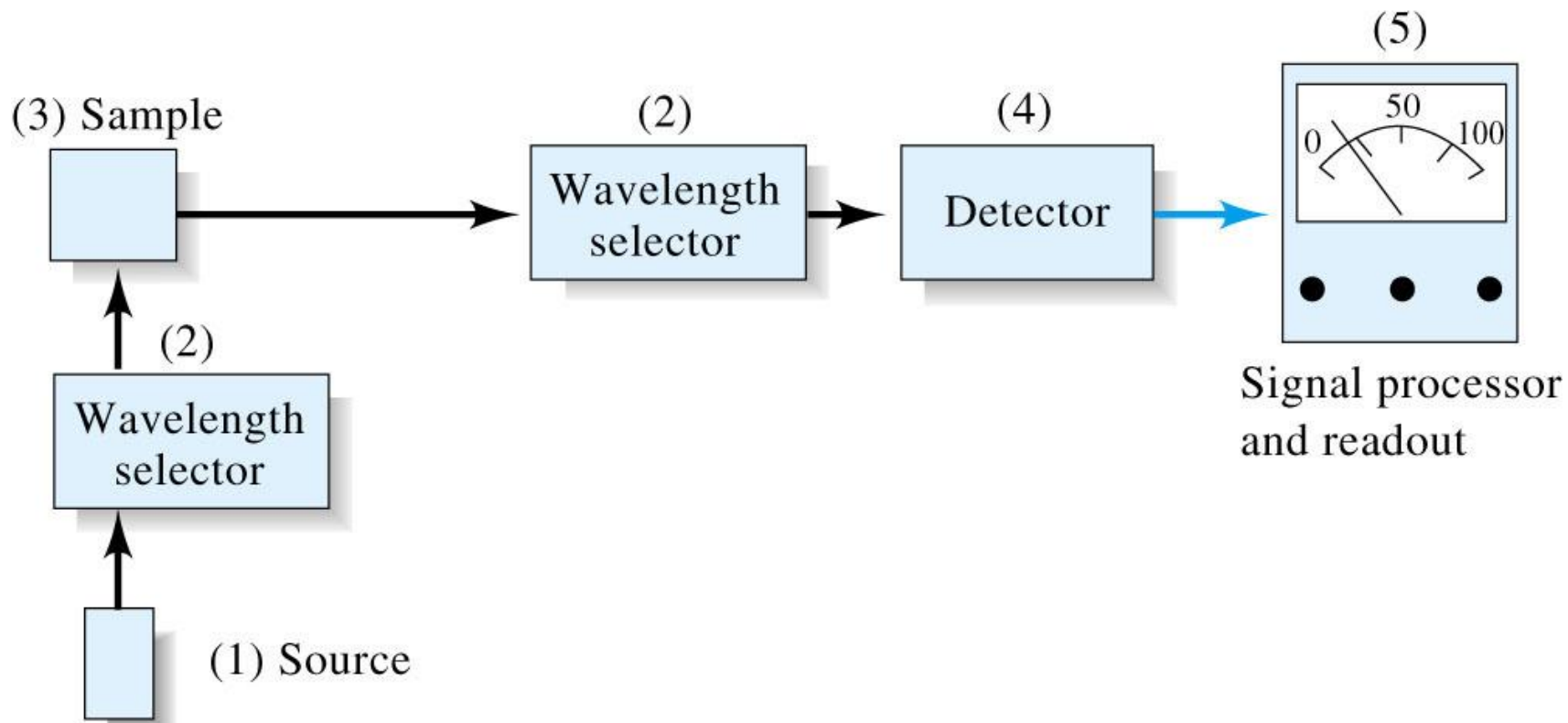
- stable source of radiant energy
- transparent container to hold sample
- device to isolate selected region of the spectrum for measurement
- detector to convert radiant energy to a signal
- signal processor and readout

# Components of Optical Instruments



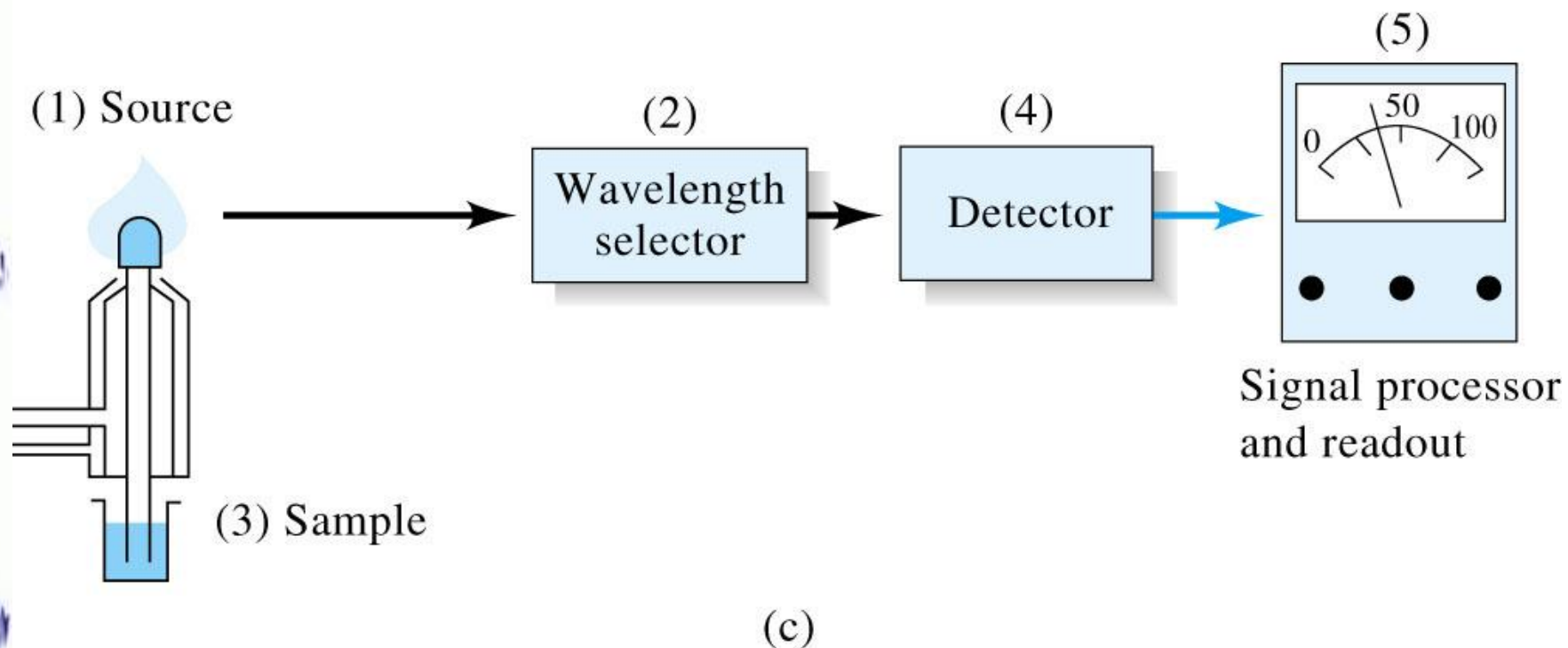
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# Components of Optical Instruments



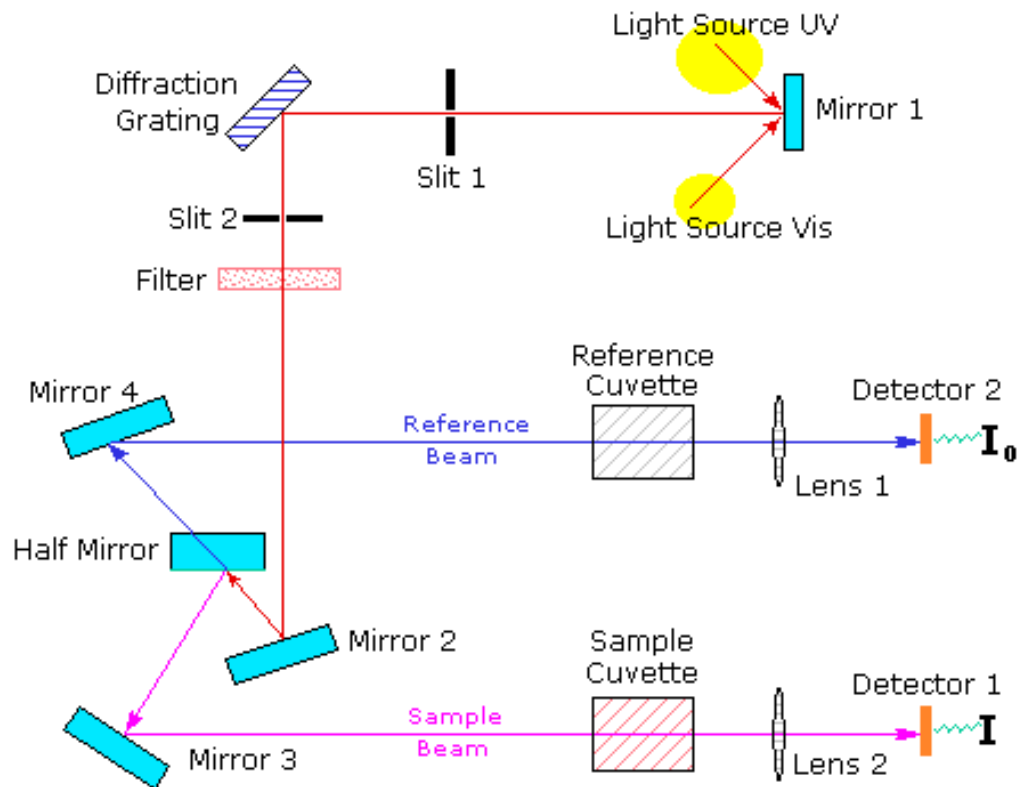
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# Components of Optical Instruments



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# Components of Optical Instruments



# Assignment

- Read Chapter 6
- Read Chapter 7
- HW2: Ch. 6: 2-12, 14, 15, 18, 19 (extra credit) (Due 1-23)
- Go over Lab Lecture 2

