



# Chemistry 4631

## Instrumental Analysis

### Lecture 13

# Molecular Luminescence Spectrometry

**When photons are absorbed, the following processes can occur:**

- **Molecular dissociation**
- **Photochemical reaction**
- **Fluorescence**
- **Phosphorescence**
- **Nonradiative return to ground state**

# Molecular Luminescence Spectrometry

## Photoluminescence

Excitation brought about by absorption of photons. Sensitive method with detection limits in parts per billion range, also has a large linear range.

- Fluorescence
- Phosphorescence

# Molecular Luminescence Spectrometry

## Theory

Typically molecular fluorescence bands are found at wavelengths longer than the resonance line. This shift to longer wavelengths (lower energies) is the Stokes shift.

# Molecular Luminescence Spectrometry

## Theory

### Electron spin

- Paired electrons have opposite spin states and thus exhibit no net magnetic field (diamagnetic) (not attracted or repelled by static magnetic fields).
- Free radicals contain unpaired electrons and have a magnetic moment and attracted to a magnetic field (paramagnetic).

# Molecular Luminescence Spectrometry

## Theory

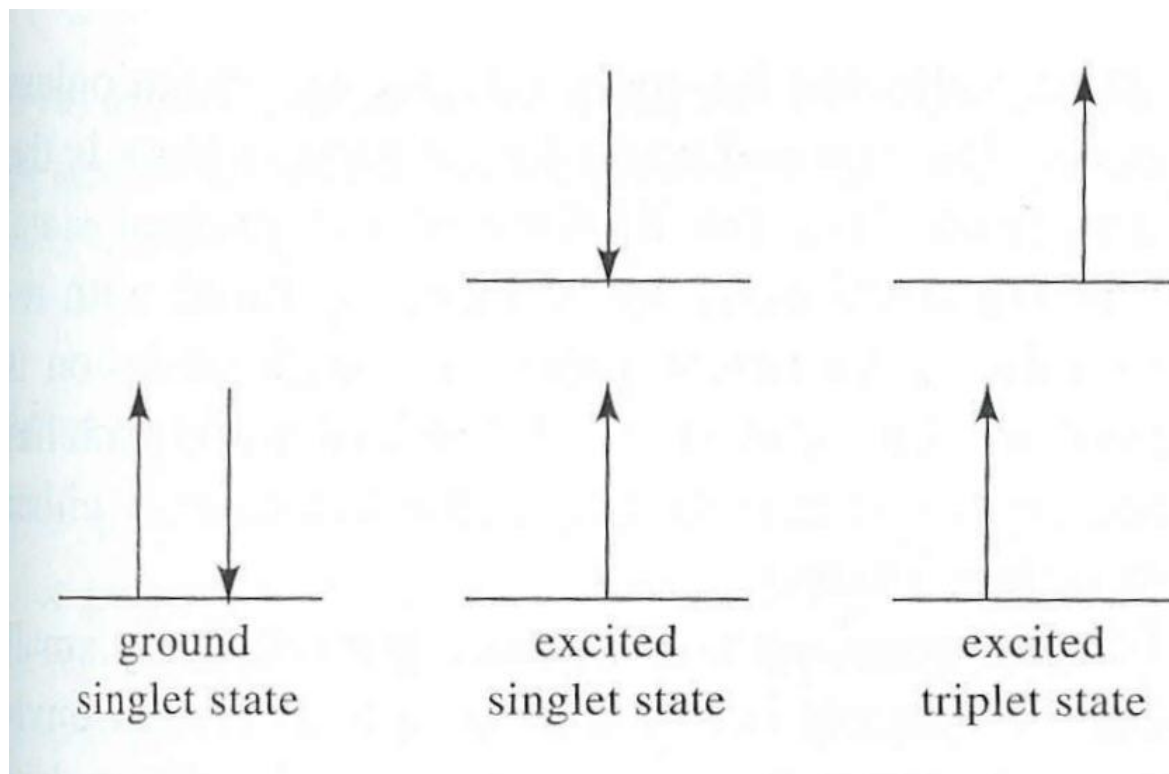
### Singlet/Triplet Excited States

- When a pair of electrons in a molecule are excited to a higher energy level, a singlet or triplet is formed.
- For the excited singlet state, the electrons are still paired, for the triplet state the spin of the electrons are unpaired.

# Molecular Luminescence Spectrometry

## Theory

### Singlet/Triplet Excited States



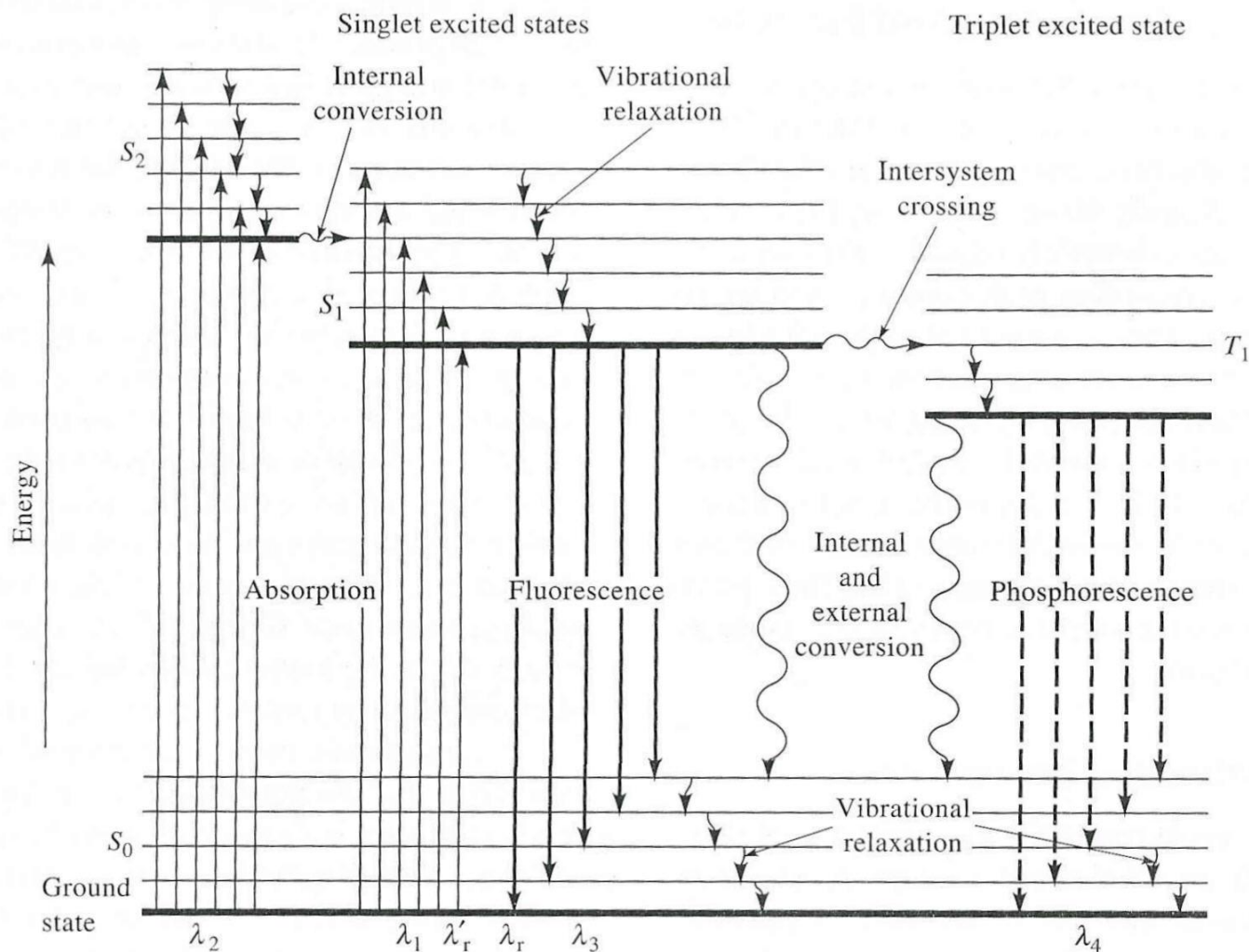
# Molecular Luminescence Spectrometry

## Theory

### Singlet/Triplet Excited States

- A singlet-triplet transition is significantly less probable than the singlet-singlet transition. The lifetime of a triplet state may range from  $10^{-4}$  to several seconds.

# Energy-level Diagrams



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

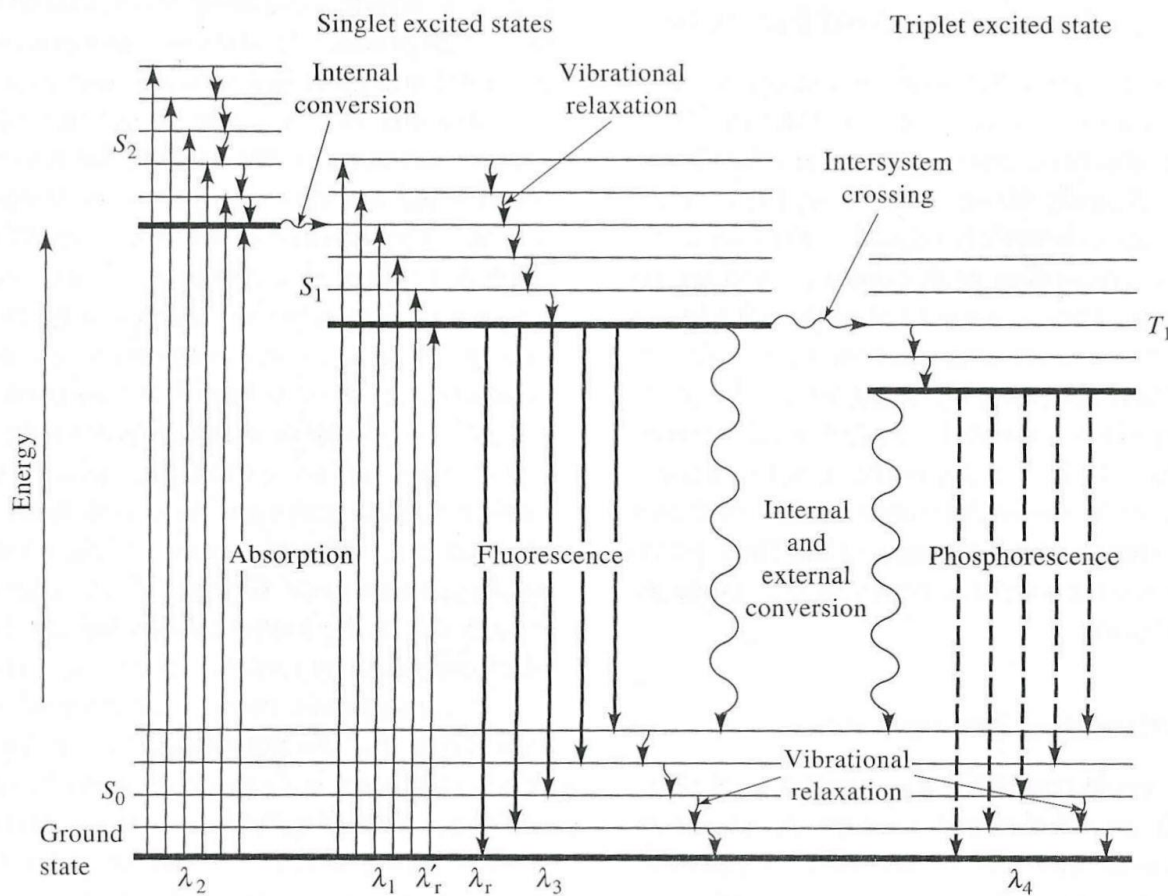
# Molecular Luminescence Spectrometry

## Internal conversion

Intermolecular process by which a molecule passes to a lower energy electronic state without emission of radiation.

The process is poorly understood but seems to occur when two electronic energy levels have overlap in vibrational energy levels. May or may not result in fluorescence.

# Molecular Luminescence Spectrometry



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

# Molecular Luminescence Spectrometry

## Vibrational Relaxation

Molecule may be promoted to several vibrational levels during the electronic excitation process, excess vibrational energy can easily be lost due to collisions of excited molecules with solvent molecules.

This process is so efficient that fluorescence must occur from lowest vibrational level of an excited electronic state.

# Molecular Luminescence Spectrometry

## Vibrational Relaxation

The result of this vibrational relaxation is to displace the fluorescence band to lower frequencies (longer  $\lambda$ 's) (Stokes shift)

# Molecular Luminescence Spectrometry

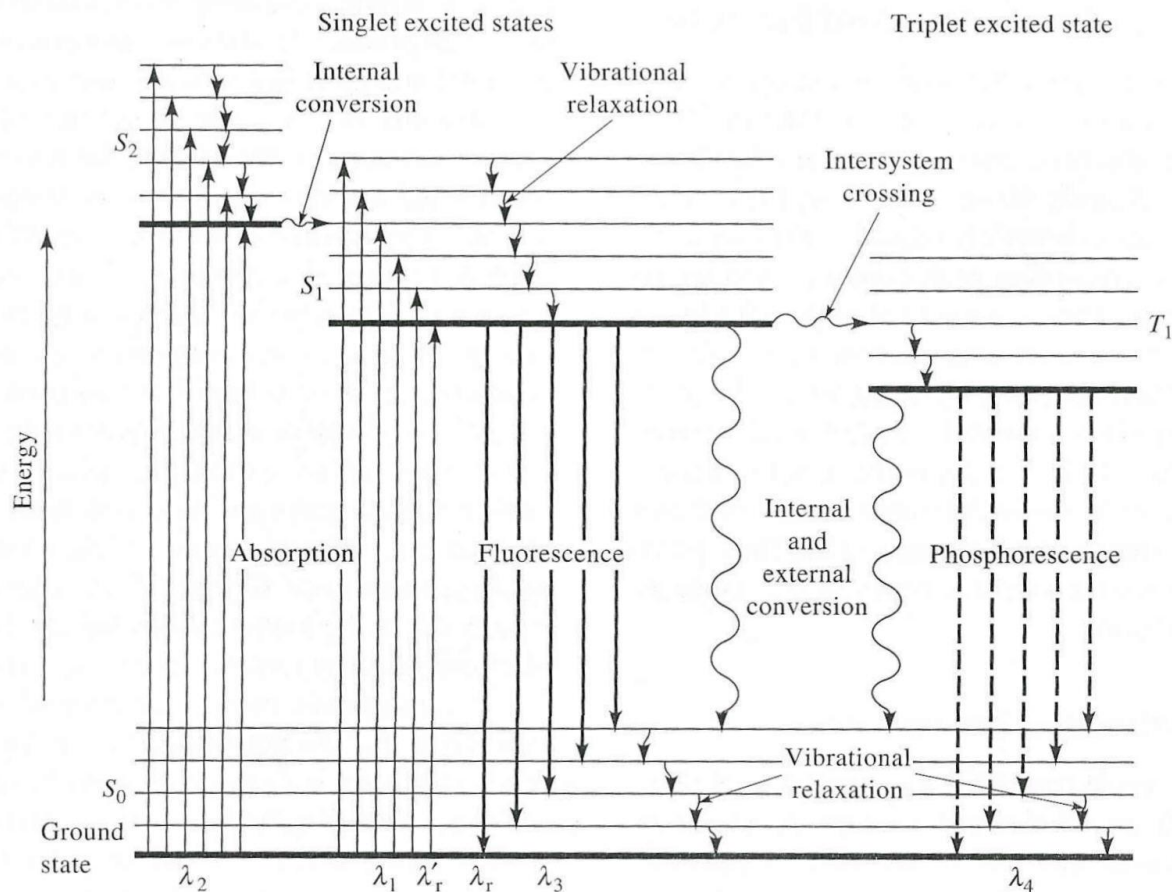


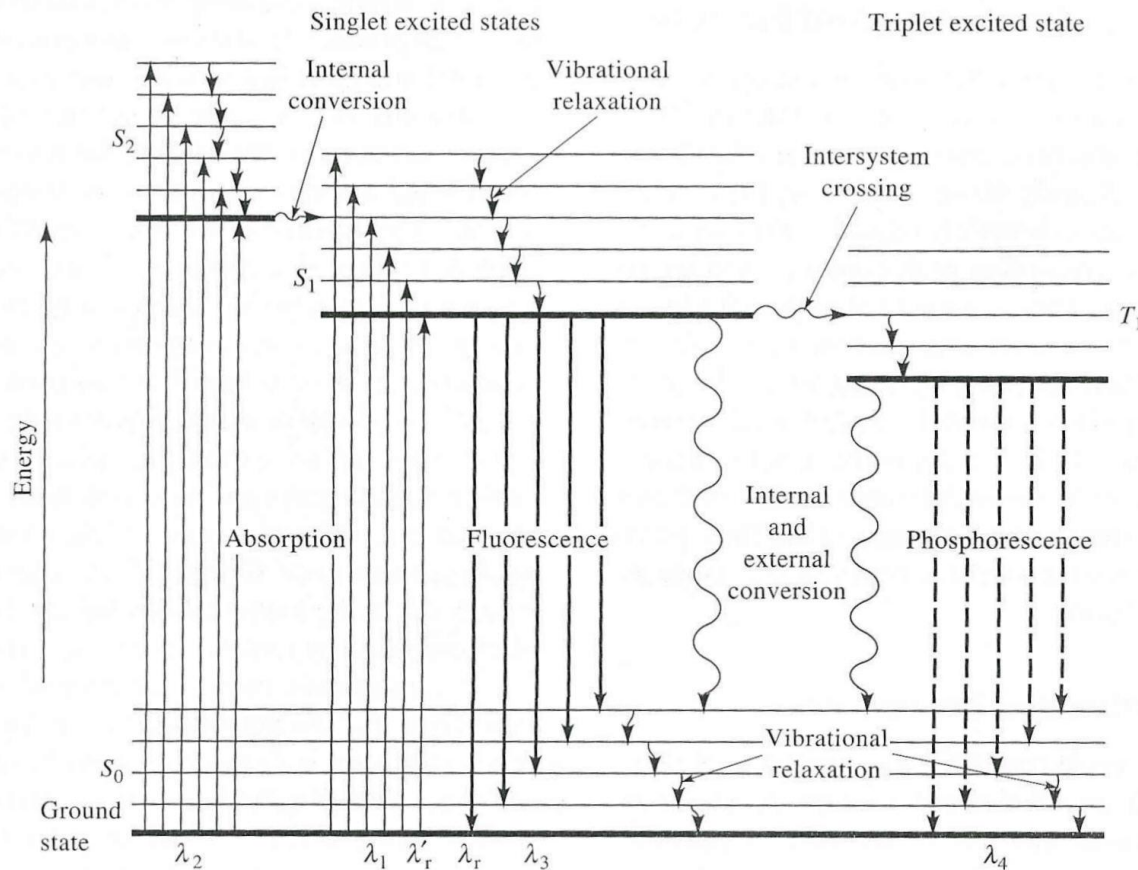
Figure 15-1 Partial energy diagram for a photoluminescent system.

# Molecular Luminescence Spectrometry

## External conversion (collisional quenching)

Energy transfer between the excited molecule and the solvent or other solutes.  
Mostly heat transfer.

# Molecular Luminescence Spectrometry



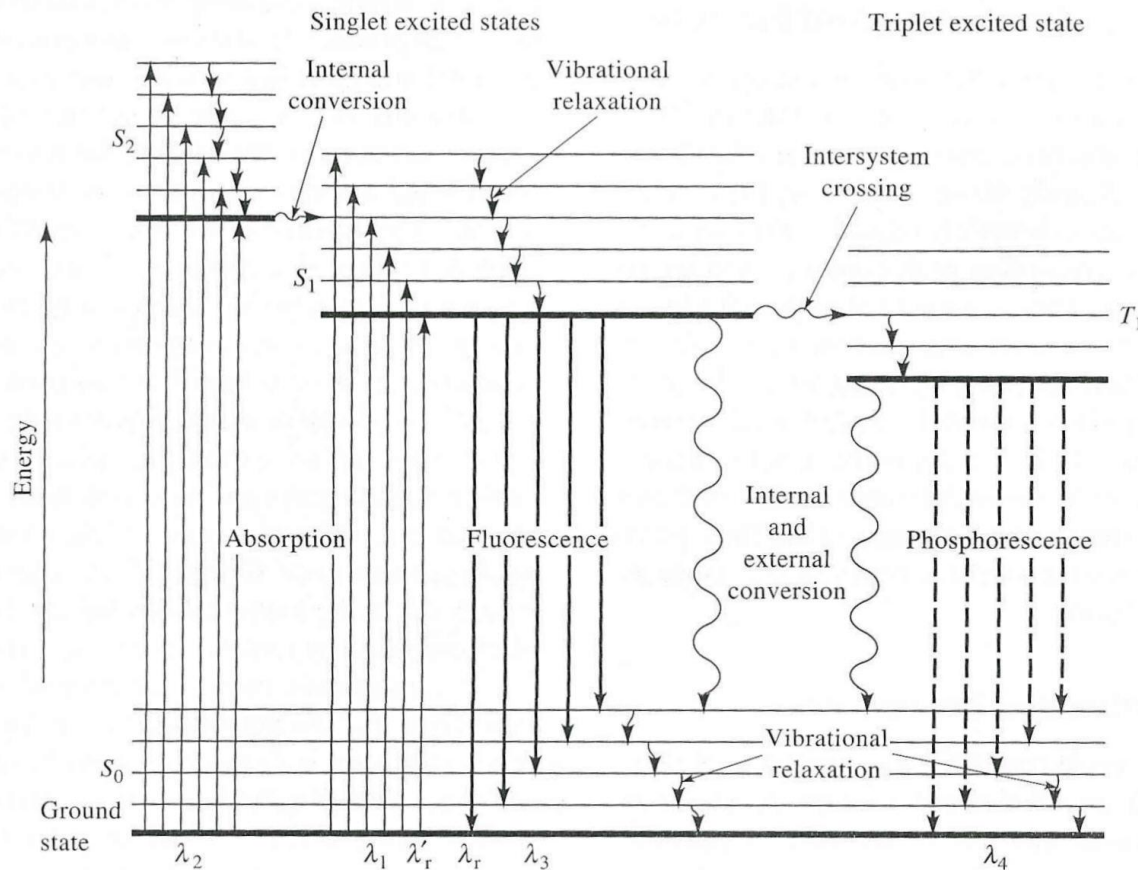
**Figure 15-1** Partial energy diagram for a photoluminescent system.

# Molecular Luminescence Spectrometry

## Intersystem crossing

Spin of an excited electron is reversed giving a change in multiplicity of the molecule. This occurs more when the vibrational levels overlap. More common in molecules having heavy atoms (i.e. I or Br)

# Molecular Luminescence Spectrometry



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

# Molecular Luminescence Spectrometry

## Deactivation Processes

Excited state dimer or self-quenching



# Molecular Luminescence Spectrometry

## Fluorescence and Phosphorescence

**Delayed fluorescence sometime confused with phosphorescence**

### **Causes of delayed fluorescence:**

- **Excimer formation**
- **Triplet-triplet annihilation**
- **Donor-acceptor interaction (anti-stokes fluorescence)**

# Molecular Luminescence Spectrometry

## Excimer formation



# Molecular Luminescence Spectrometry

## Triplet-triplet annihilation



# Molecular Luminescence Spectrometry

## Donor-acceptor interaction (anti-stokes fluorescence)



# Molecular Luminescence Spectrometry

## Transition type

Fluorescence seldom seen for  $\lambda$ 's lower than 250 nm, because at these  $\lambda$ '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

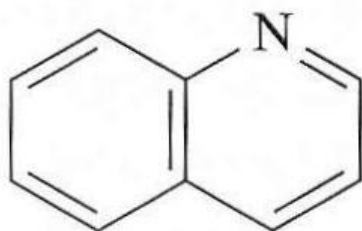
## Structure

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

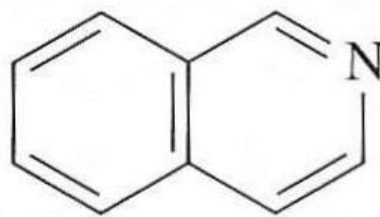
# Molecular Luminescence Spectrometry

## Structure

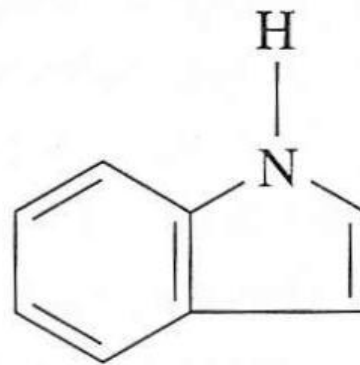
Fluorescence higher with increasing number of rings.



quinoline



isoquinoline



indole

# Molecular Luminescence Spectrometry

**Substitution on the rings also affect fluorescence:**

**Groups with non-bonding electrons enhance fluorescence**

**-NH<sub>2</sub>, -OH, -F, -OCH<sub>3</sub>, -NHR and -NR<sub>2</sub>**

**Groups with electron withdrawing groups quench fluorescence**

**-COOH, -NO<sub>2</sub>, -NH-CO-CH<sub>3</sub>, -Cl, -Br, -I**

# Molecular Luminescence Spectrometry

TABLE 15-1 Effect of Substitution on the Fluorescence of Benzene<sup>a</sup>

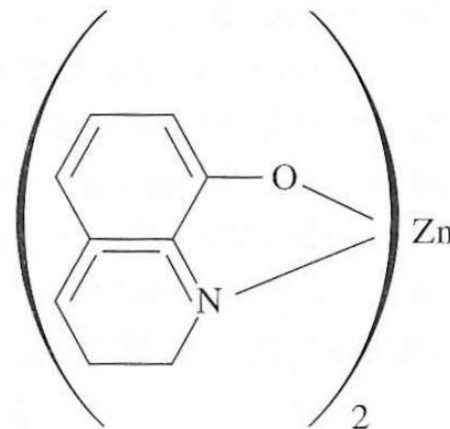
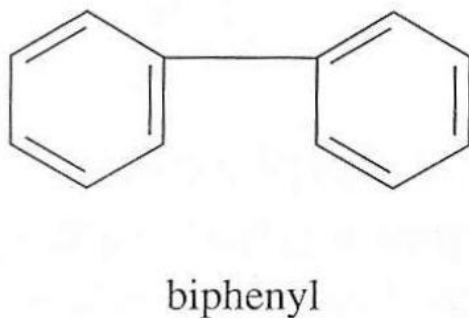
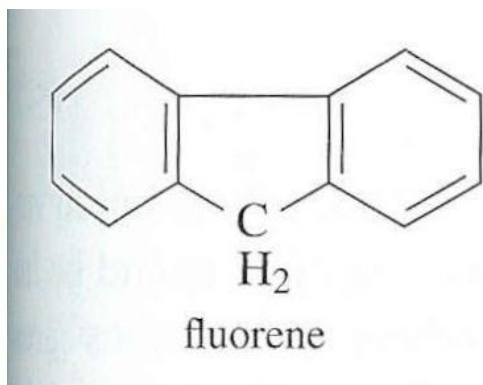
Compound	Formula	Wavelength of Fluorescence, nm	Relative Intensity of Fluorescence
Benzene	C <sub>6</sub> H <sub>6</sub>	270–310	10
Toluene	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	270–320	17
Propylbenzene	C <sub>6</sub> H <sub>5</sub> C <sub>3</sub> H <sub>7</sub>	270–320	17
Fluorobenzene	C <sub>6</sub> H <sub>5</sub> F	270–320	10
Chlorobenzene	C <sub>6</sub> H <sub>5</sub> Cl	275–345	7
Bromobenzene	C <sub>6</sub> H <sub>5</sub> Br	290–380	5
Iodobenzene	C <sub>6</sub> H <sub>5</sub> I	—	0
Phenol	C <sub>6</sub> H <sub>5</sub> OH	285–365	18
Phenolate ion	C <sub>6</sub> H <sub>5</sub> O <sup>-</sup>	310–400	10
Anisole	C <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub>	285–345	20
Aniline	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	310–405	20
Anilinium ion	C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> <sup>+</sup>	—	0
Benzoic acid	C <sub>6</sub> H <sub>5</sub> COOH	310–390	3
Benzonitrile	C <sub>6</sub> H <sub>5</sub> CN	280–360	20
Nitrobenzene	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	—	0

<sup>a</sup>In ethanol solution.

# Molecular Luminescence Spectrometry

## Effects on Fluorescence

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



# Molecular Luminescence Spectrometry

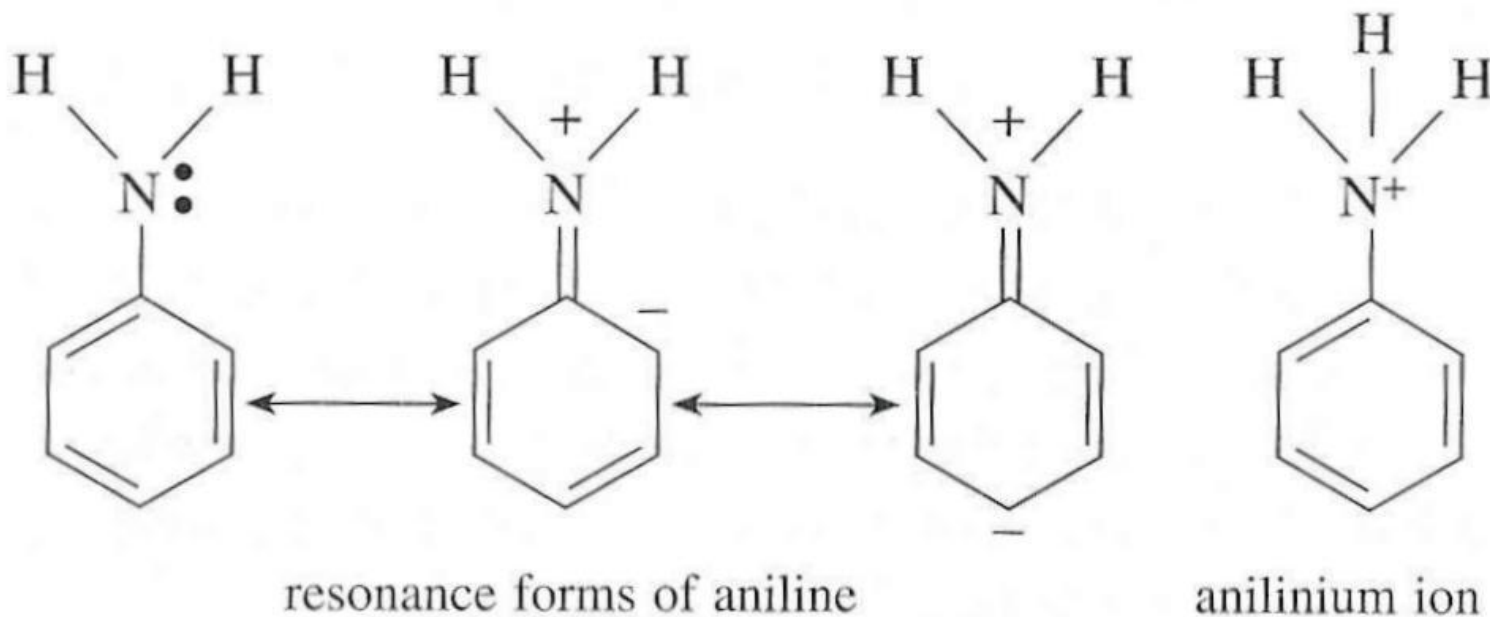
## Effects on Fluorescence

- **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



# Molecular Luminescence Spectrometry

**Quantum yield –**

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

# Molecular Luminescence Spectrometry

## Quantitative Analysis using Fluorescence

$$F = I_0 \phi_F f(\theta) g(\lambda) (1 - e^{-\epsilon bc})$$

$\phi_F$  - quantum efficiency

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

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

# Molecular Luminescence Spectrometry

## Quantitative Analysis using Fluorescence

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

$$F = 2.3 I_0 \phi_F f(\theta) g(\lambda) e^{-\epsilon bc}$$

# Assignment

- Read Chapter 15
- Homework 5 Chapter 15: 1, 2, 4, 5, 9, 13
- HW5 Chapter 15 due 2-20

