Chemistry 4631

Instrumental Analysis

Lecture 11

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

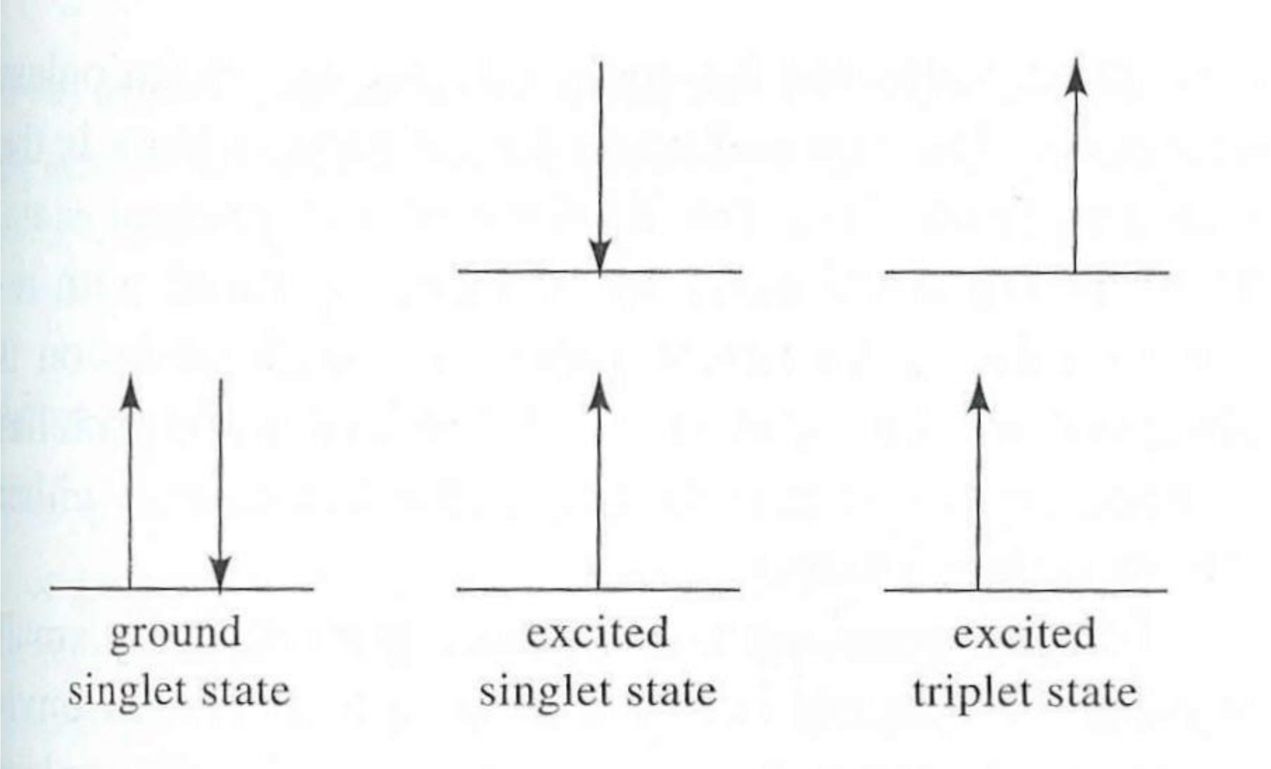
Singlet/Triplet Excited States

- 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

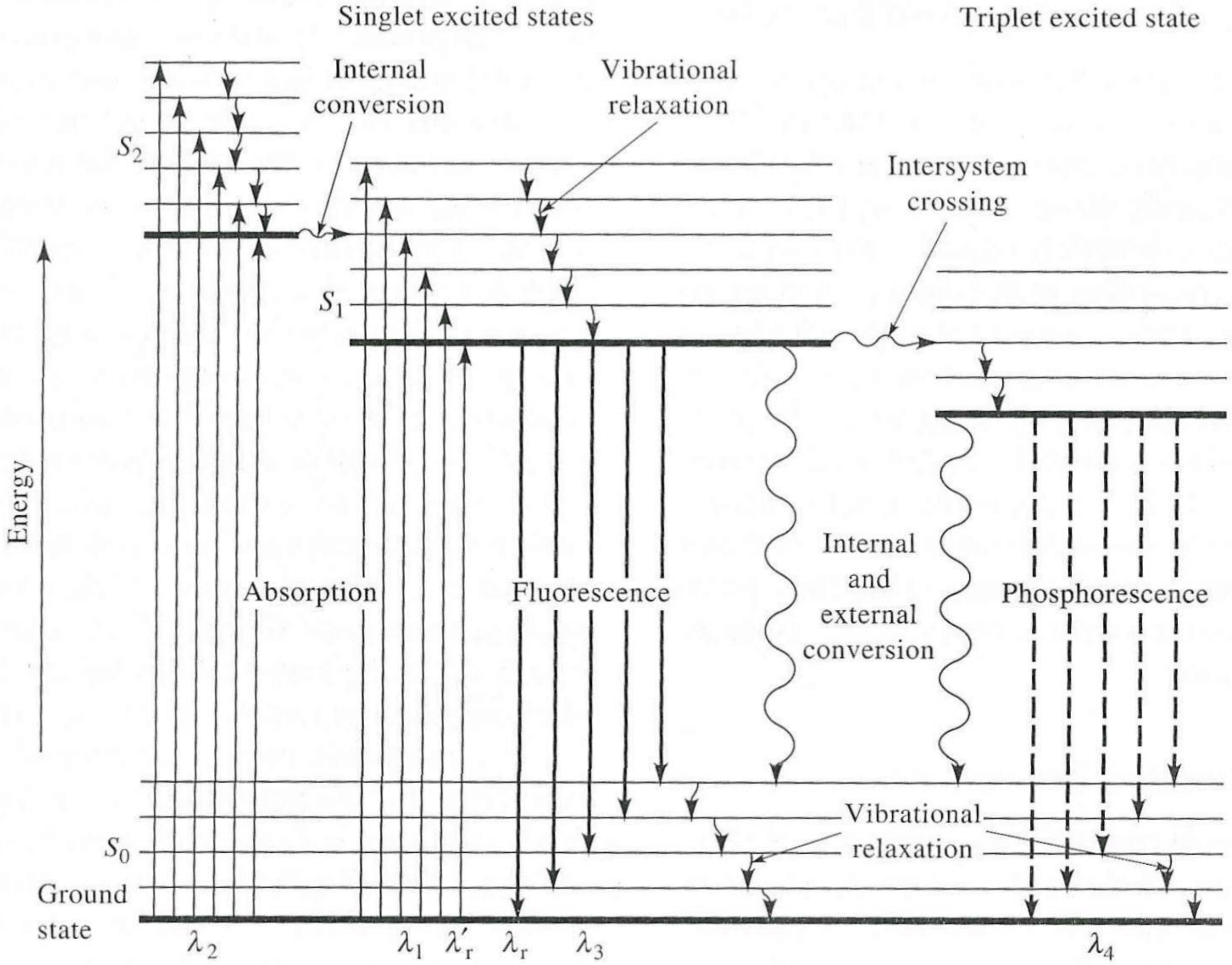


Figure 15-1 Partial energy diagram for a photoluminescent system.

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

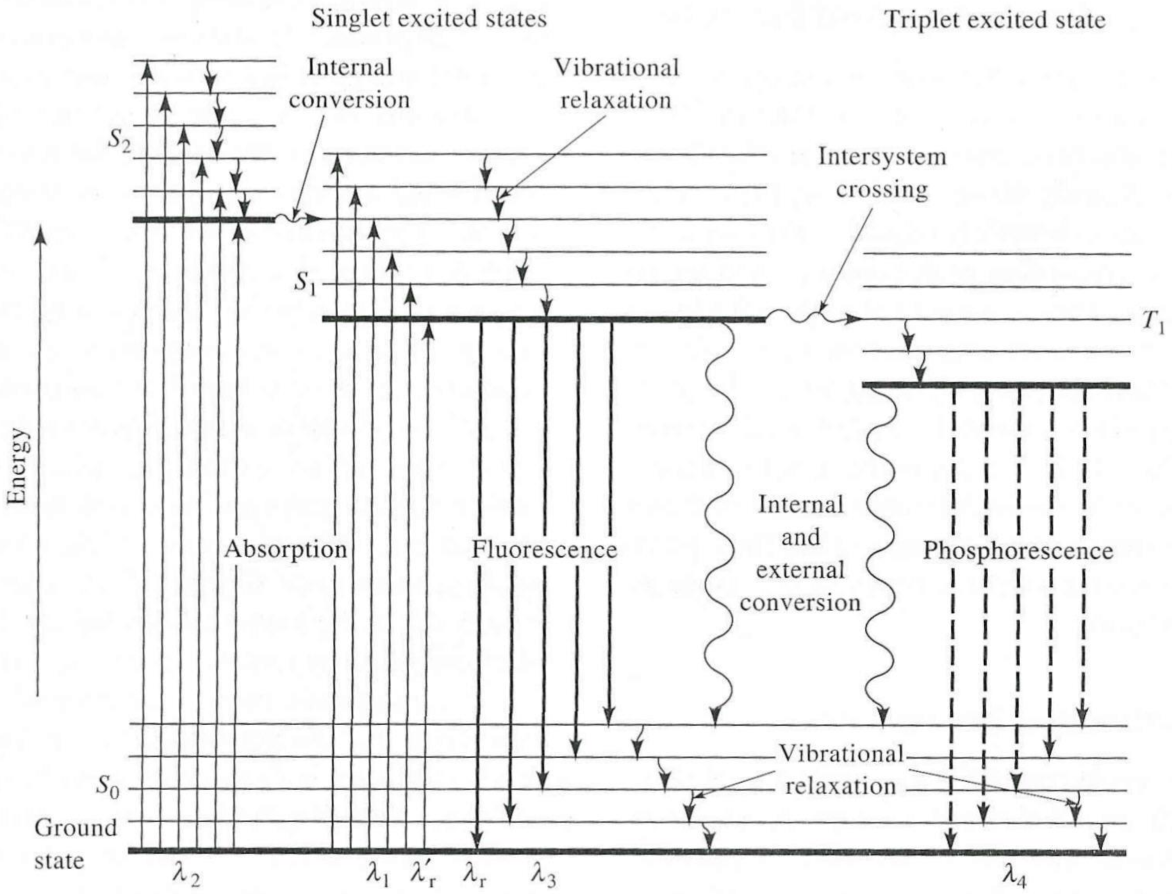


Figure 15-1 Partial energy diagram for a photoluminescent system.

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 λ's) (Stokes shift)

Molecular Luminescence Spectrometry

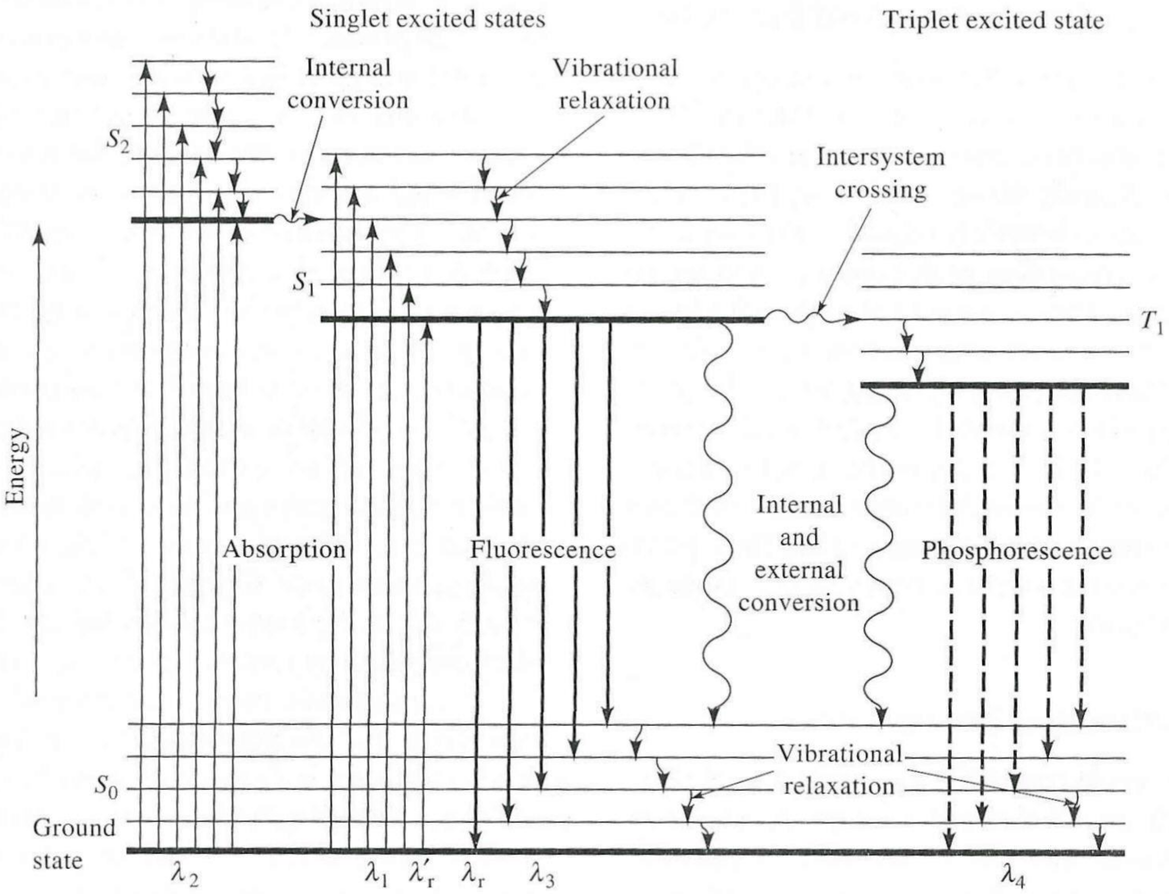


Figure 15-1 Partial energy diagram for a photoluminescent system.

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

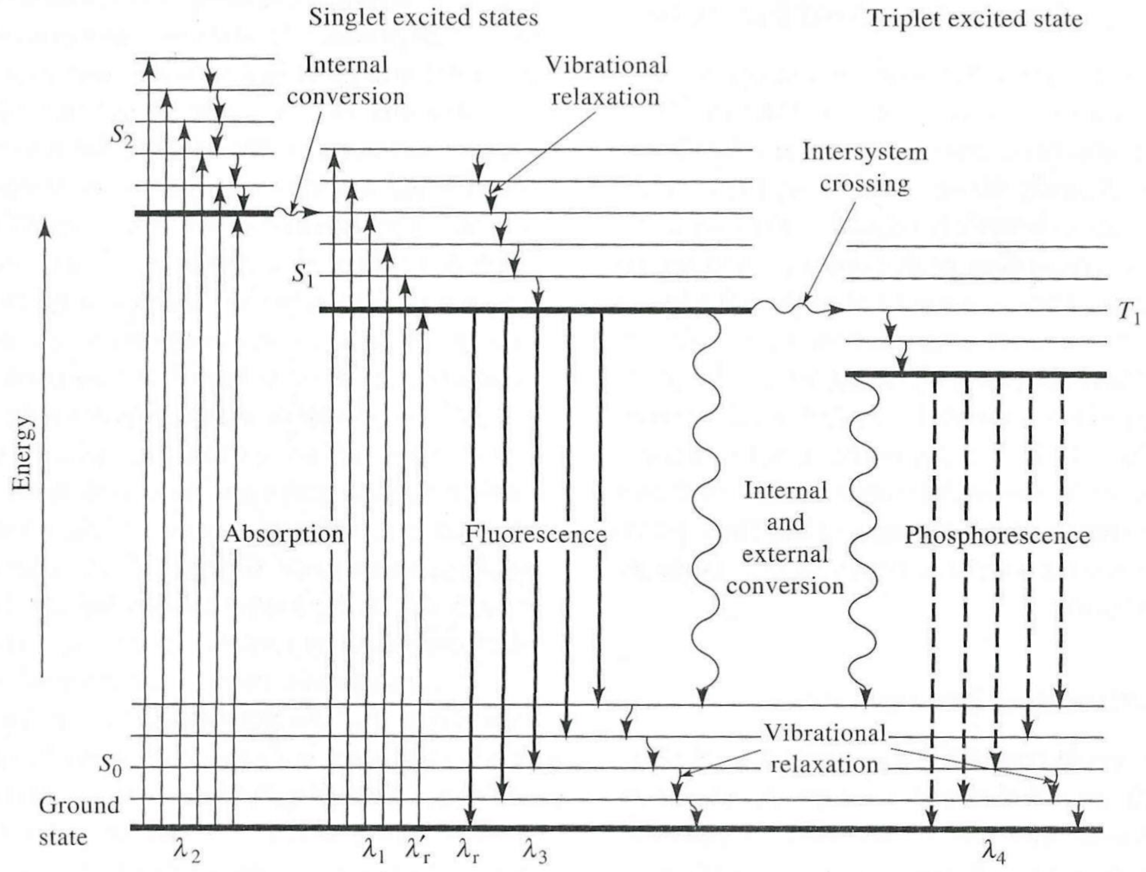


Figure 15-1 Partial energy diagram for a photoluminescent system.

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

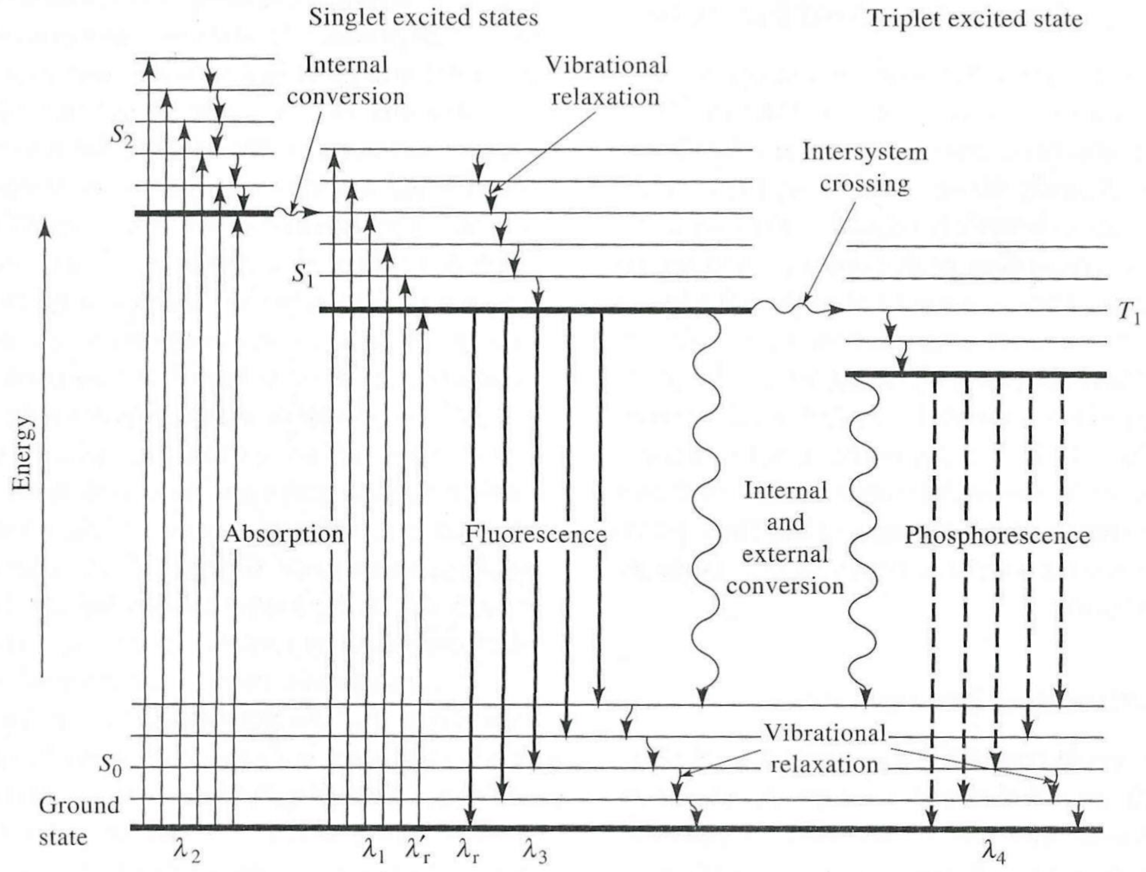


Figure 15-1 Partial energy diagram for a photoluminescent system.

Molecular Luminescence Spectrometry

Deactivation Processes

Excited state diamer or self-quenching

$$A^* + A \rightarrow AA^* \rightarrow 2A + \text{heat}$$

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

$A + hv_1 \rightarrow A^*$

$A^* + A \leftrightarrow AA^*$

$AA^* \rightarrow A^* + A$

$A^* \rightarrow A + hv_2$

Molecular Luminescence Spectrometry

Triplet-triplet annihilation

$A + hv_1 \rightarrow A^{*1}$

$A^{*1} \rightarrow A^{*3}$

$A^{*3} + A^{*3} \rightarrow A + A^{*1}$

$A^{*1} \rightarrow A + hv_2$

Molecular Luminescence Spectrometry

Donor-acceptor interaction (anti-stokes fluorescence)

$D + h\nu_1 \rightarrow D^{*1}$

$D^{*1} \rightarrow D^{*3}$

$D^{*3} + A \rightarrow A^{*3} + D$

$A^{*3} + D^{*3} \rightarrow A^{*1} + D$

$A^{*1} \rightarrow A + h\nu_2$

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

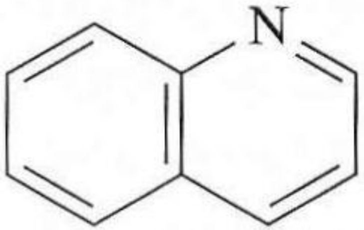
Structure

Fluorescence more common in compounds having aromatic functional groups with low energy π → π* transition levels.

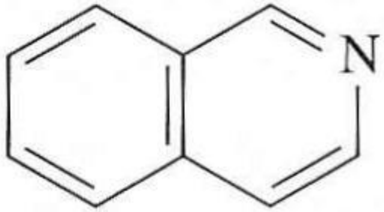
Molecular Luminescence Spectrometry

Structure

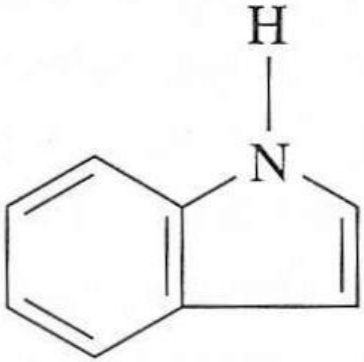
- Fluorescence higher with increasing number of rings.



quinoline



isoquinoline



indole

Molecular Luminescence Spectrometry

Substitution on the rings also affect fluorescence:

Groups with non-bonding electrons enhance fluorescence

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

Groups with electron withdrawing groups quench fluorescence

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

Molecular Luminescence Spectrometry

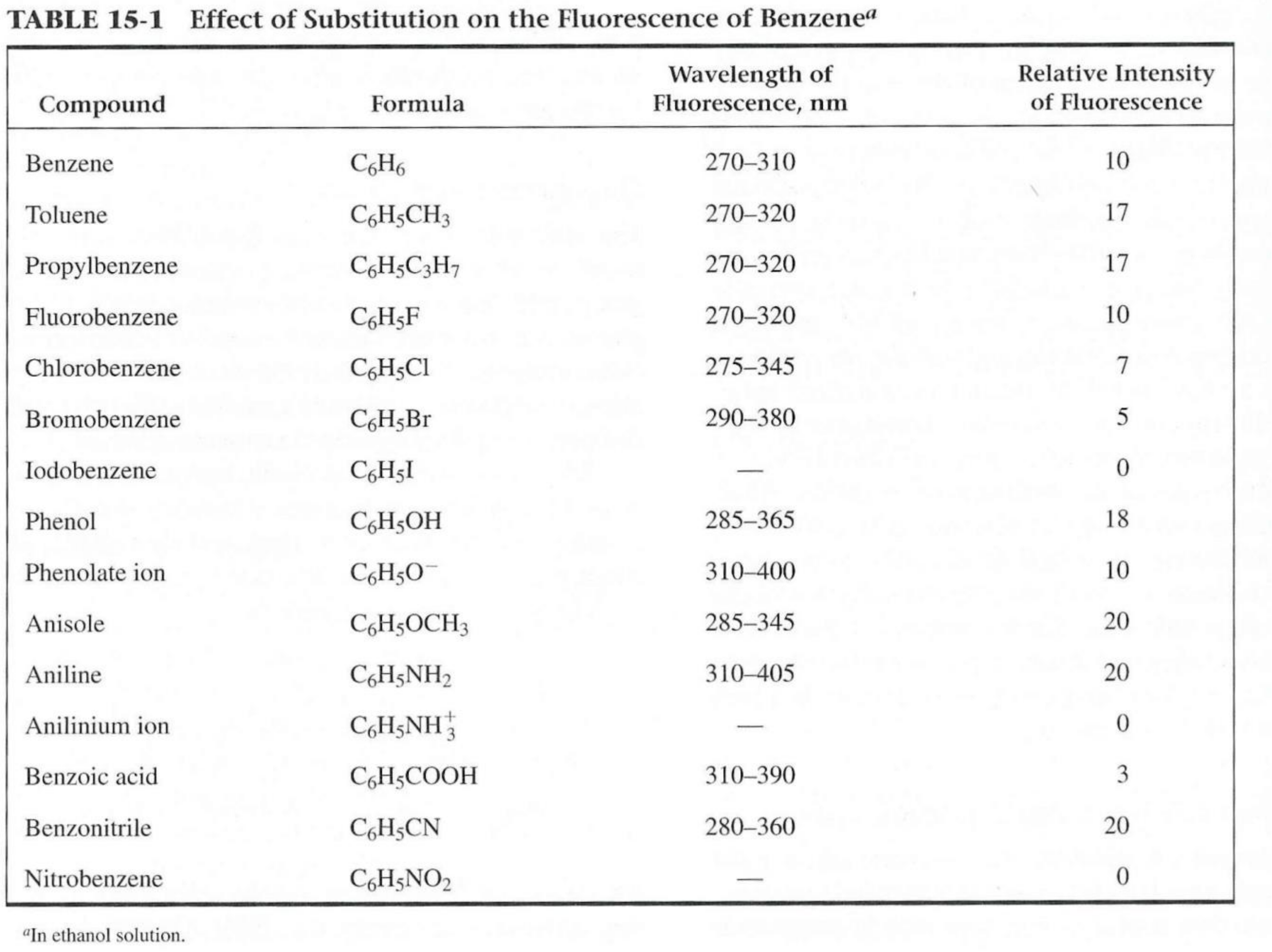


TABLE 15-1 Effect of Substitution on the Fluorescence of Benzene[a]

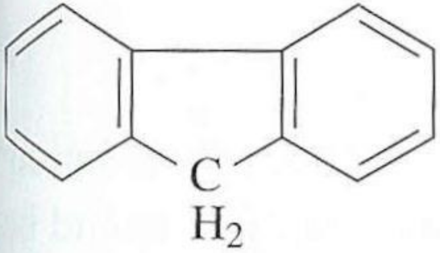
Compound	Formula	Wavelength of Fluorescence, nm	Relative Intensity of Fluorescence
Benzene	C_6H_6	270–310	10
Toluene	$C_6H_5CH_3$	270–320	17
Propylbenzene	$C_6H_5C_3H_7$	270–320	17
Fluorobenzene	C_6H_5F	270–320	10
Chlorobenzene	C_6H_5Cl	275–345	7
Bromobenzene	C_6H_5Br	290–380	5
Iodobenzene	C_6H_5I	—	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.

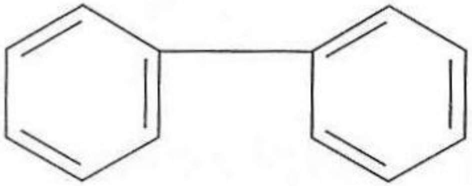
Molecular Luminescence Spectrometry

Effects on Fluorescence

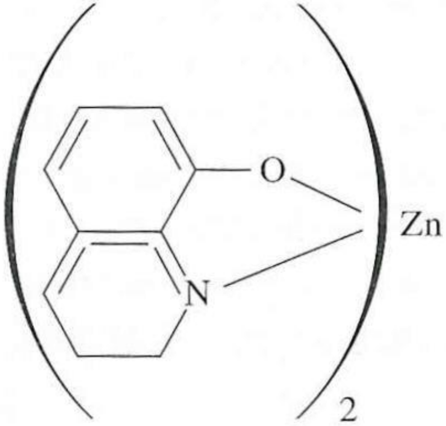
- Very rigid structures are more likely to fluorescence.
- Complexing will increase fluorescence.



fluorene



biphenyl



Molecular Luminescence Spectrometry

Effects on Fluorescence

- Fluorescence decreases with increasing temperature – more collisions.

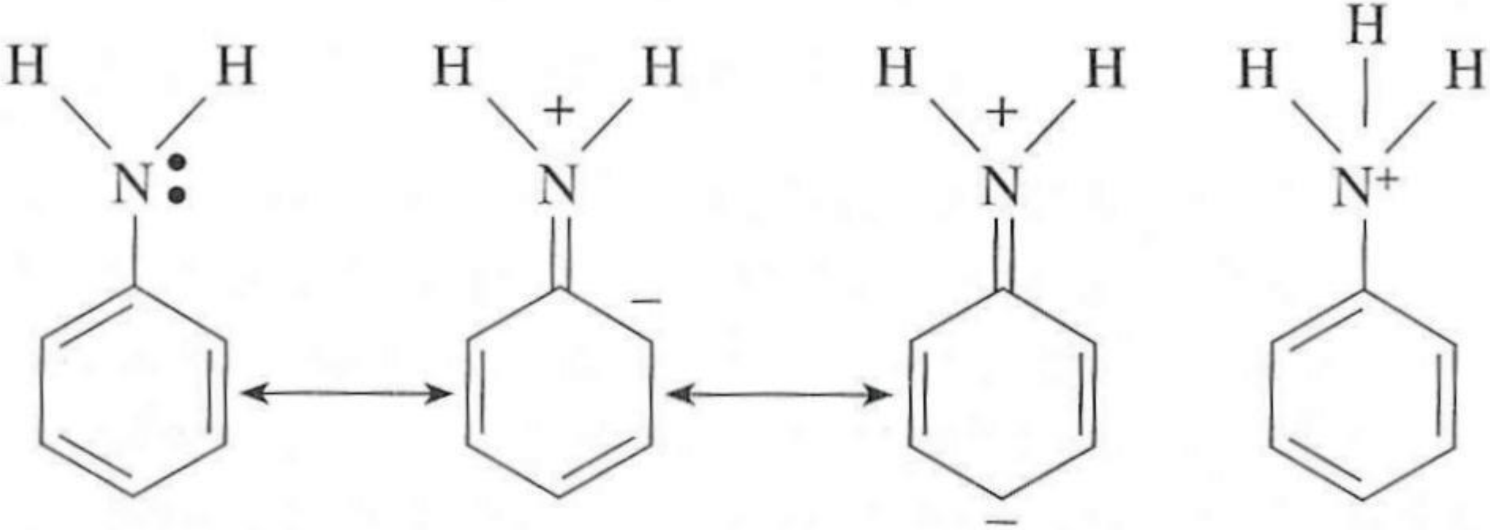
- Fluorescence decreases with solvents containing heavy atoms, (increases rate of triplet formation).

- 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°)

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

Molecular Luminescence Spectrometry

Quantitative Analysis using Fluorescence

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

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

Assignment

- Read Chapter 15
- Homework Chapter 15: 1, 2, 4, 5, 9, 13
- HW5 Chapter 15 due 2/27/23
- Test 2- Lectures 8 to 14 - Friday March 10th