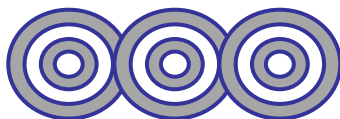




Instrumental Methods of Analysis



Molecular Photoluminescence Spectroscopy

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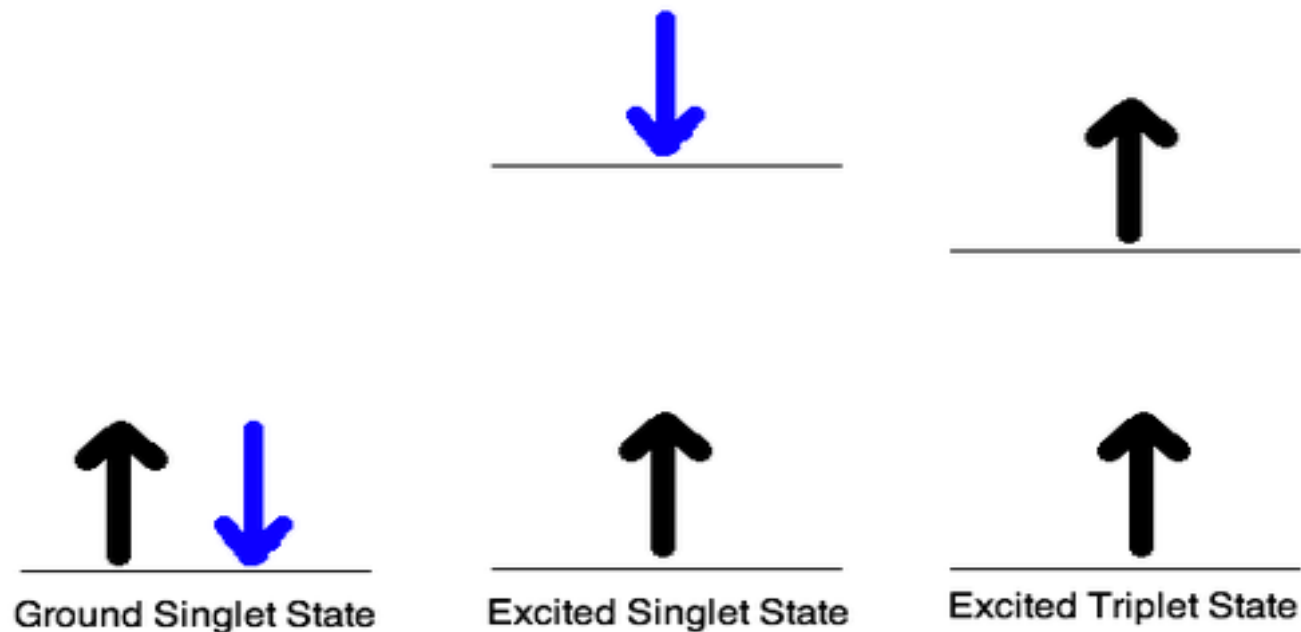


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Photoluminescence is divided into two categories:

- **Fluorescence.**
- **Phosphorescence.**



singlet excited state

An excited state in which all electron spins are paired.

triplet excited state

An excited state in which unpaired electron spins occur.

-Absorption of an ultraviolet or visible photon promotes a valence electron from its ground state to an excited state with conservation of the electron's spin (**singlet excited state**).

-Emission of a photon from a singlet excited state to a singlet ground state, or between any two energy levels with the same spin, is called **fluorescence**.

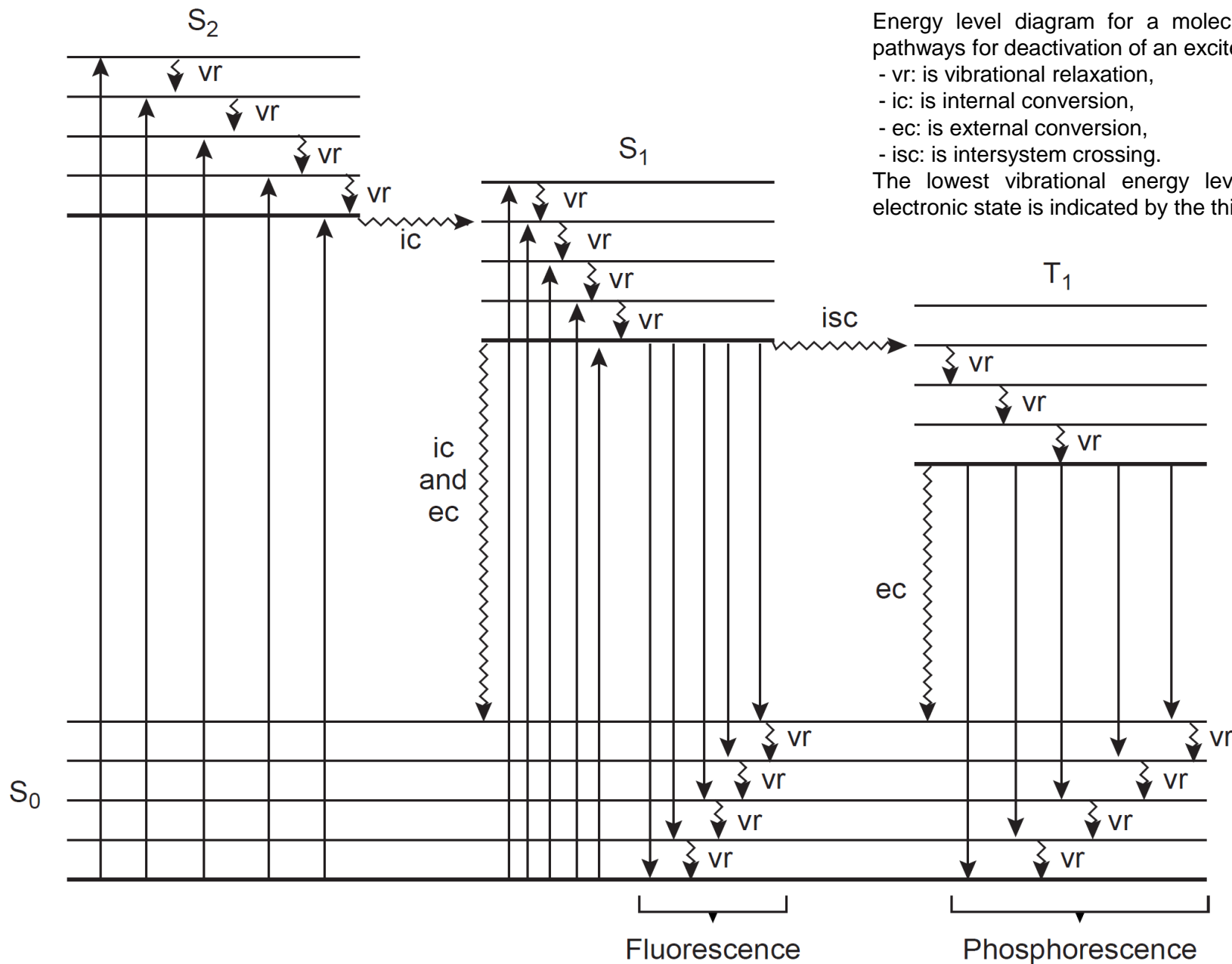
-The average lifetime of the electron in the excited state is only 10^{-5} – 10^{-8} s.

-In some cases an electron in a singlet excited state is transformed to a **triplet excited state** in which its spin is no longer paired with that of the ground state.

-Emission between a triplet excited state and a singlet ground state, or between any two energy levels that differ in their respective spin states, is called **phosphorescence**.

-Because the average lifetime for phosphorescence ranges from 10^{-4} to 10^4 s, phosphorescence may continue for some time after removing the excitation source.

Molecular fluorescence and phosphorescence spectra



Energy level diagram for a molecule showing pathways for deactivation of an excited state:

- vr: is vibrational relaxation,
- ic: is internal conversion,
- ec: is external conversion,
- isc: is intersystem crossing.

The lowest vibrational energy level for each electronic state is indicated by the thicker line.

The ground state, is a singlet state labeled S_0 . Absorption of a photon of correct energy excites the molecule to one of several vibrational energy levels in the first excited electronic state, S_1 , or the second electronic excited state, S_2 , both of which are **singlet states**.

Relaxation to the ground state from these excited states occurs by a number of mechanisms that are either;

- **Radiationless (no photons are emitted) or**
- **Involve the emission of a photon.**

The most likely pathway by which a molecule relaxes back to its ground state is that which gives the shortest lifetime for the excited state (by the fastest mechanism).

Radiationless Deactivation

Vibrational relaxation:

in which a molecule in an excited vibrational energy level loses energy as it moves to a lower vibrational energy level in the same electronic state. Vibrational relaxation is very rapid, with the molecule's average lifetime in an excited vibrational energy level being 10^{-12} s or less.

Internal conversion:

in which a molecule in the ground vibrational level of an excited electronic state passes directly into a high vibrational energy level of a lower energy electronic state of the same spin state.

External conversion:

in which excess energy is transferred to the solvent or another component in the sample matrix.

Intersystem crossing:

in which a molecule in the ground vibrational energy level of an excited electronic state passes into a high vibrational energy level of a lower energy electronic energy state with a different spin state.

Radiation Deactivation

(Fluorescence & Phosphorescence)

Fluorescence:

Fluorescence occurs when a molecule in the lowest vibrational energy level of an excited electronic state returns to a lower energy electronic state by emitting a photon.

Fluorescence may return the molecule to any of several vibrational energy levels in the ground electronic state. Fluorescence, therefore, occurs over a range of wavelengths. Because the change in energy for fluorescent emission is generally less than that for absorption, a molecule's fluorescence spectrum is shifted to higher wavelengths than its absorption spectrum.

Fluorescence is generally observed with molecules where the lowest energy absorption is a ($\pi \rightarrow \pi^*$) transition, although some ($n \rightarrow \pi^*$) transitions show weak fluorescence.

Phosphorescence:

Phosphorescence occurs when a molecule in the lowest vibrational energy level of an excited triplet electronic state returns to a lower-energy state with the opposite spin as the higher-energy state by emitting a photon.

Phosphorescence is most favorable for molecules that have ($n \rightarrow \pi^*$) transitions, which have a higher probability for an intersystem crossing than do ($\pi \rightarrow \pi^*$) transitions.

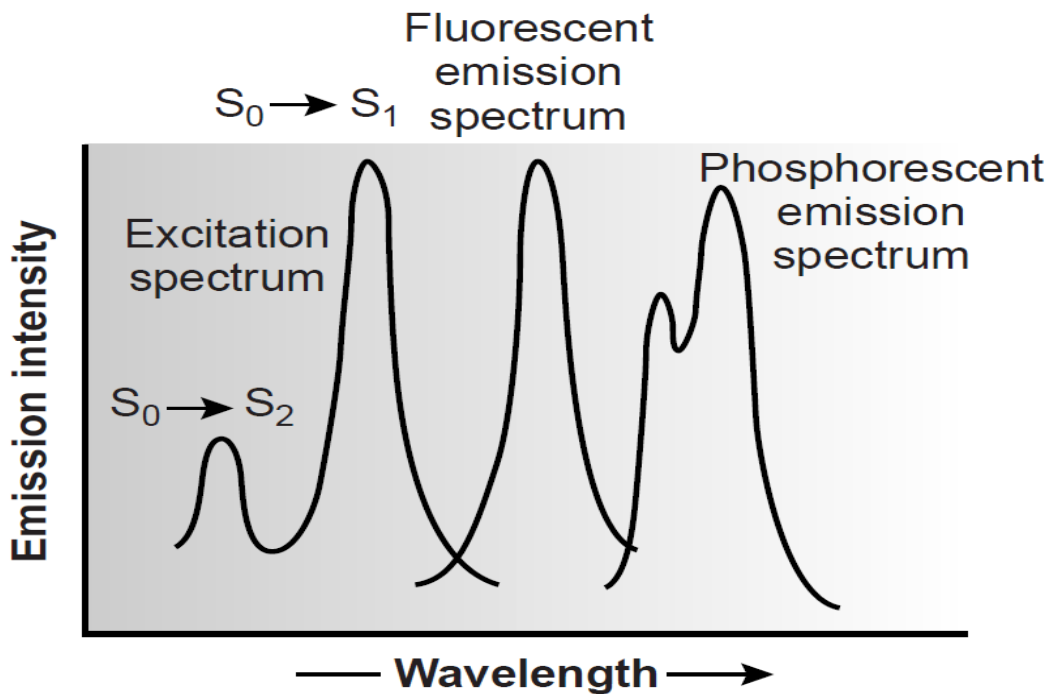
Excitation and Emission Spectra

Photoluminescence spectra are recorded by measuring the intensity of emitted radiation as a function of either the excitation or emission wavelength.

An **excitation spectrum** is obtained by monitoring emission at a fixed wavelength while varying the excitation wavelength.

When corrected for variations in source intensity and detector response, a sample's excitation spectrum is nearly identical to its absorbance spectrum.

In an **emission spectrum** a fixed wavelength is used to excite the molecules, and the intensity of emitted radiation is monitored as a function of wavelength.



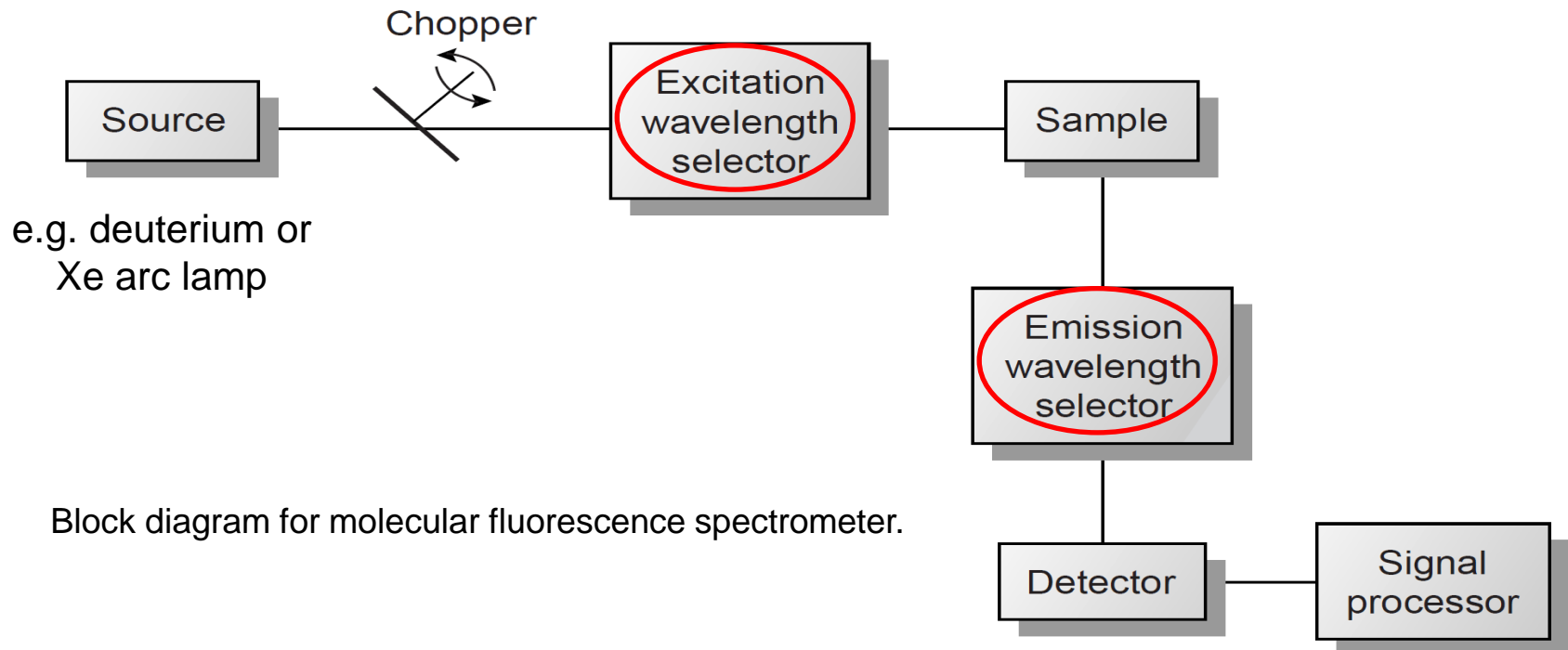
Example of molecular excitation and emission spectra.

Instrumentation

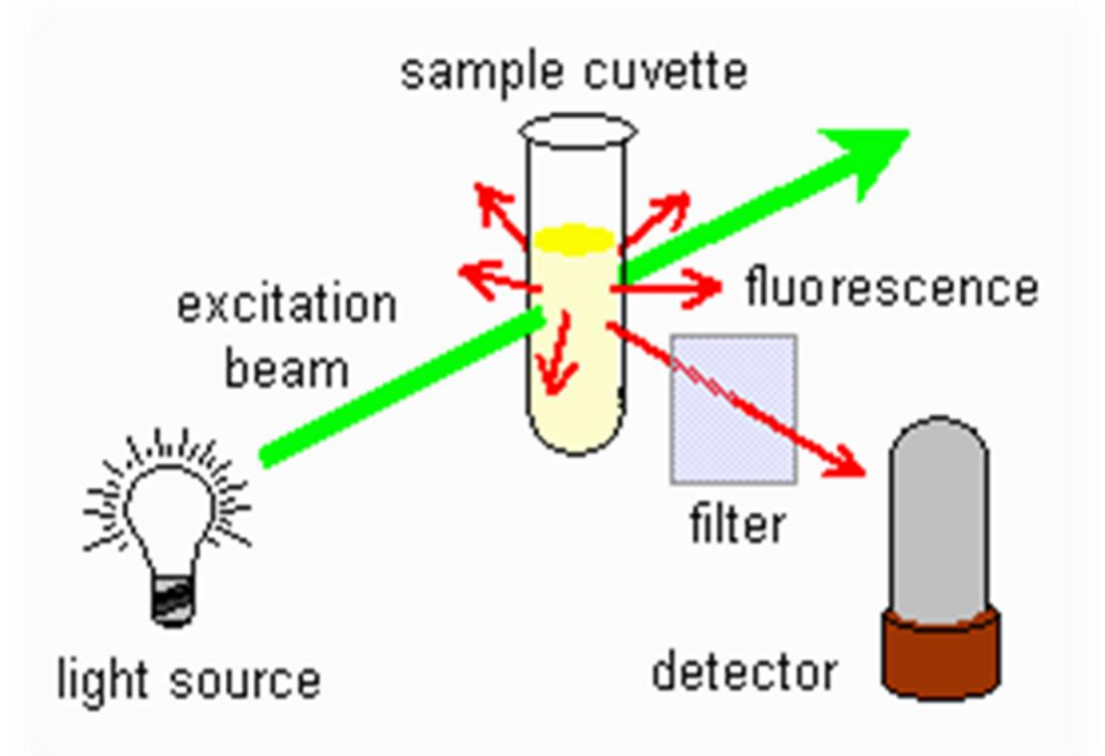
The basic design of instrumentation for monitoring molecular fluorescence and molecular phosphorescence is similar to that found for other spectroscopies.

Molecular Fluorescence

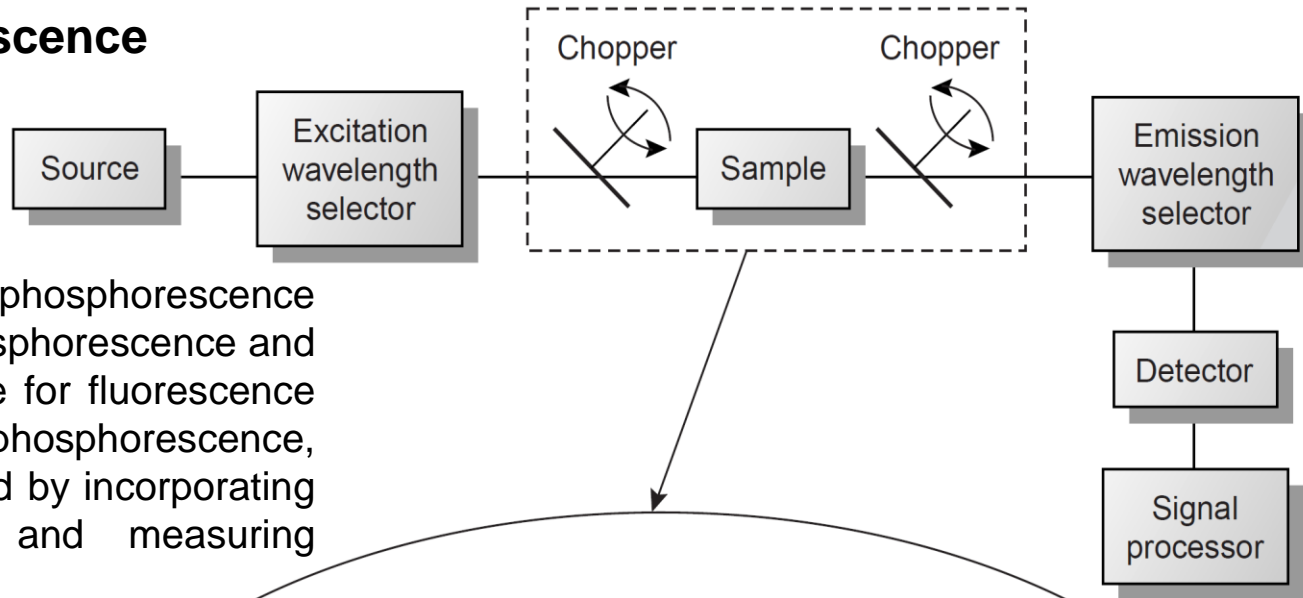
A typical fluorimeter contains an excitation source, sample cell, fluorescence detector.



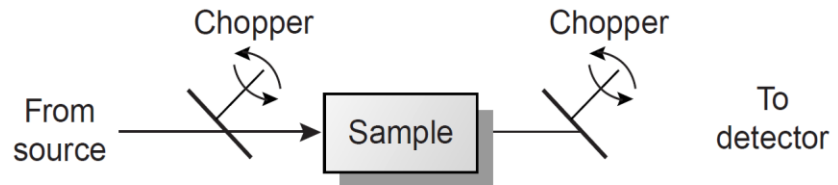
In contrast to instruments for absorption spectroscopy, the optical paths for the source and detector are usually positioned at an angle of 90° .



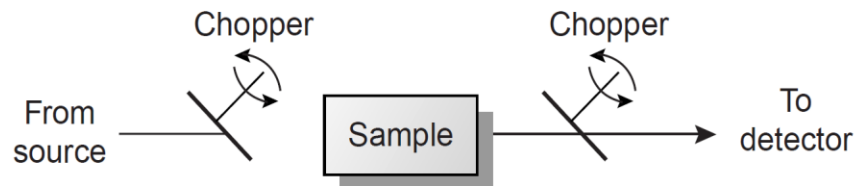
Molecular Phosphorescence



(a) Excitation



(b) Emission



Instrumentation for molecular phosphorescence must discriminate between phosphorescence and fluorescence. Since the lifetime for fluorescence is much shorter than that for phosphorescence, discrimination is easily achieved by incorporating a delay between exciting and measuring phosphorescent emission.

Block diagram for molecular phosphorescence spectrometer with inset showing how choppers are used to isolate excitation and emission.

