Optical spectroscopic techniques

Absorption spectroscopy in the UV and visible region.
(See in the Manuel LIGHT ABSORPTION)

Absorption spectroscopy uses the phenomenon of light absorption for qualitative and quantitative analysis of **dilute solutions**.

The loss of intensity due to the absorption of the incident light is a phenomenon that obeys the general law of intensity loss:

$$J = J_0 e^{-\mu x} .$$

μ is the absorption coefficient.
The measure of absorptivity can be expressed in transmittance (T):

$$T = \frac{J}{J_0} .$$

A more commonly used term is the absorbance (A) or optical density (OD), which can be defined as:

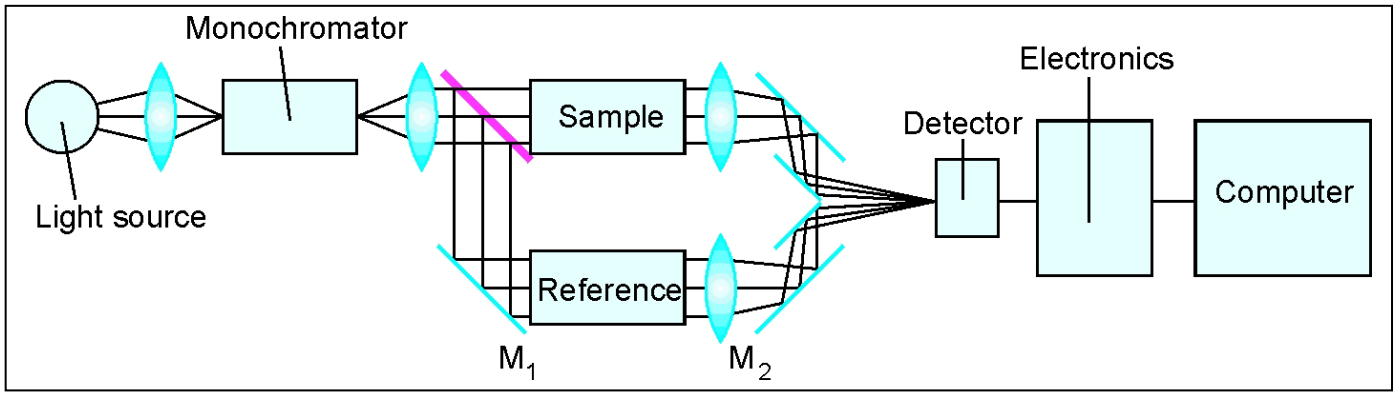
$$A = \log\left(\frac{J_0}{J}\right).$$

Lambert-Beer law

$$A = \varepsilon(\lambda) c l ,$$

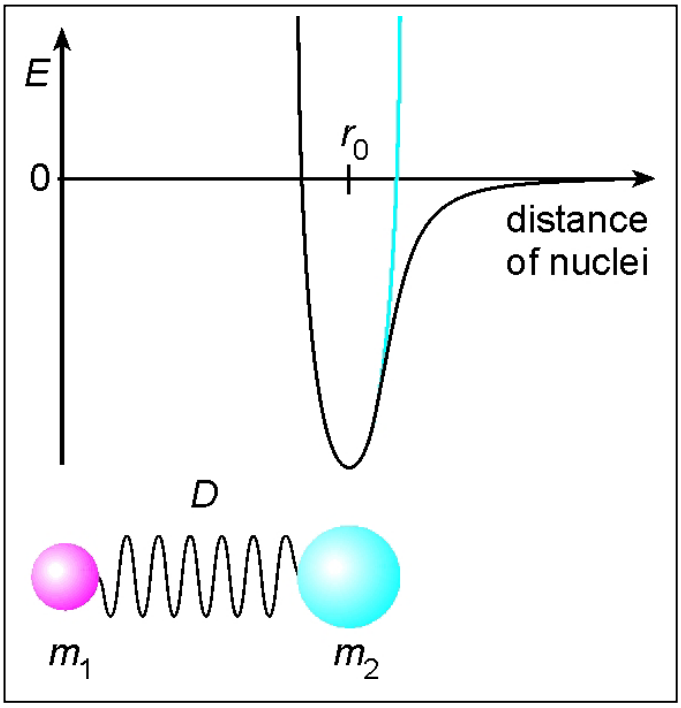
where $\varepsilon(\lambda)$ is molar extinction coefficient, l is the thickness of the cuvette that contains the solution and c is the concentration of the solution. (Linear proportionality)

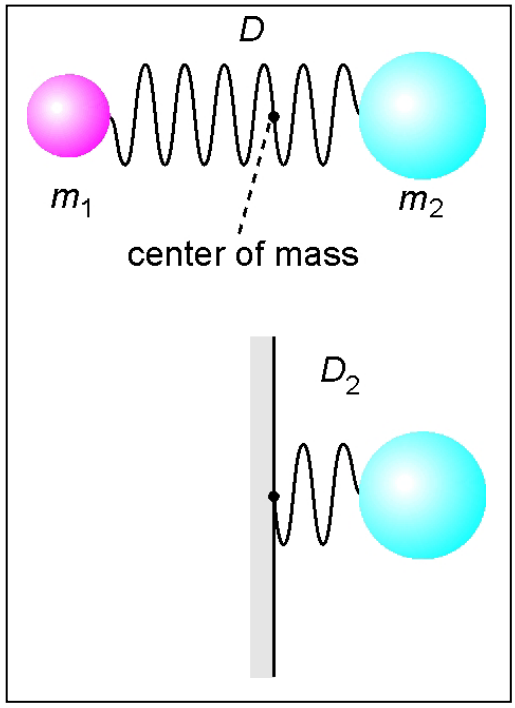
Absorption spectrophotometers



Infrared spectroscopy

Background:



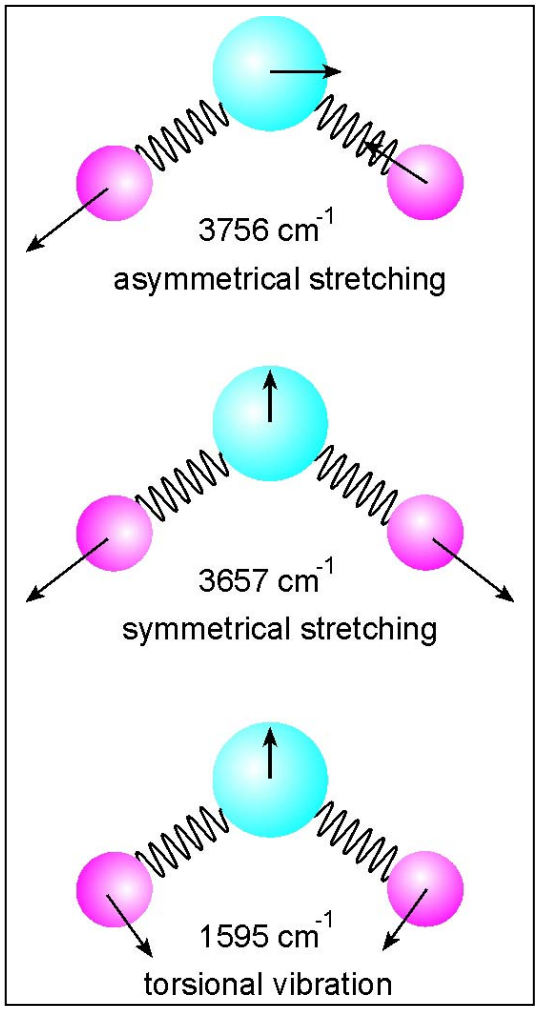


Potential energy of a diatomic molecule as a function of the distance of the two nuclei

$$f = \frac{1}{2\pi}\sqrt{\frac{D_2}{m_2}} = \frac{1}{2\pi}\sqrt{D\frac{m_1+m_2}{m_1 m_2}}$$

Molecular vibrations
The independent vibrations are called **normal modes**.
(3*N*-6 degree of freedom)

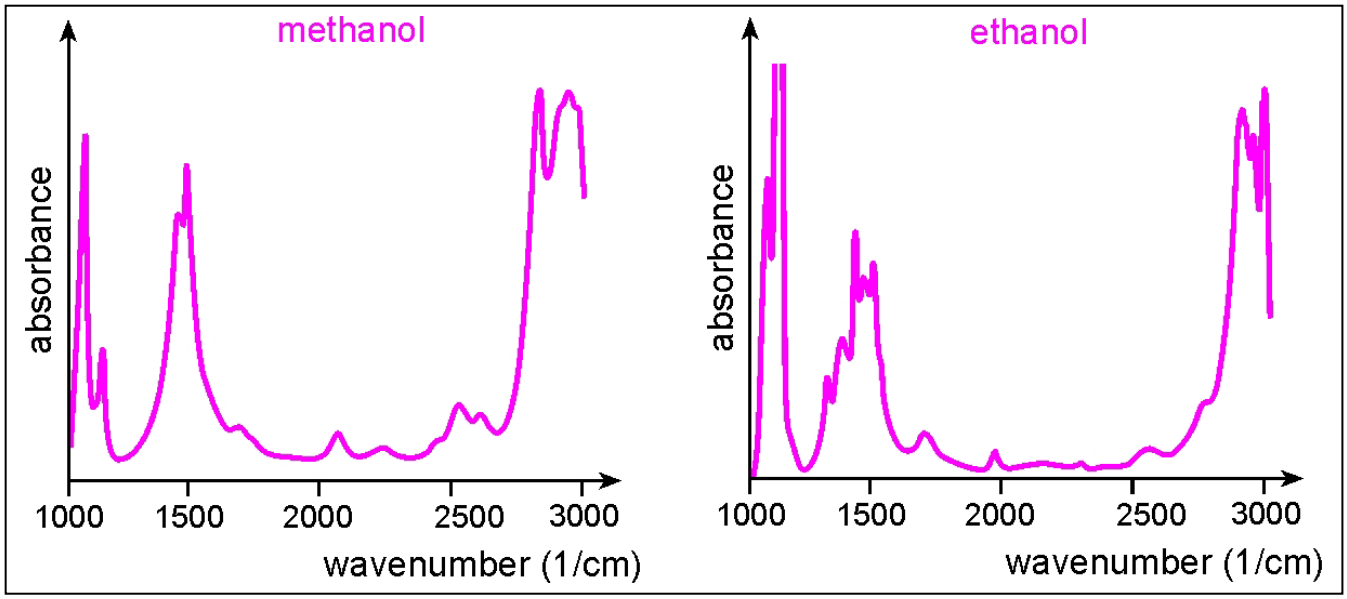
Figure: normal vibrations of water



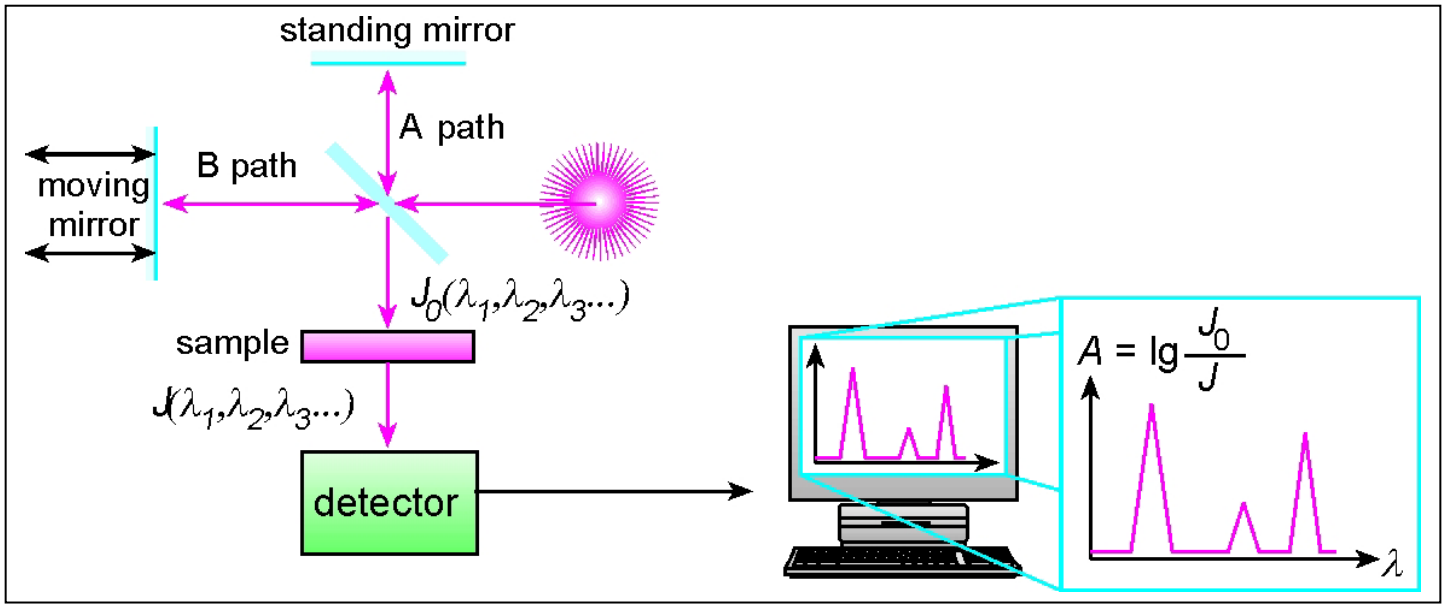
The typical vibrational frequencies fall within the range of 10-100 THz. Photons of this energy fall in the 3-30 μm wavelength range.
(350-3500 cm^{-1})

Identification of molecules and chemicals, analytical applications of IR spectroscopy

The 1100-1700 cm^{-1} region of the infrared spectrum is called fingerprint region as vibrations that are characteristic of the molecular structure fall into this region. These spectral lines as the name indicates uniquely characterize the molecules therefore they can be used for analytical purposes.



Fourier transformed infrared (FTIR) spectrophotometer

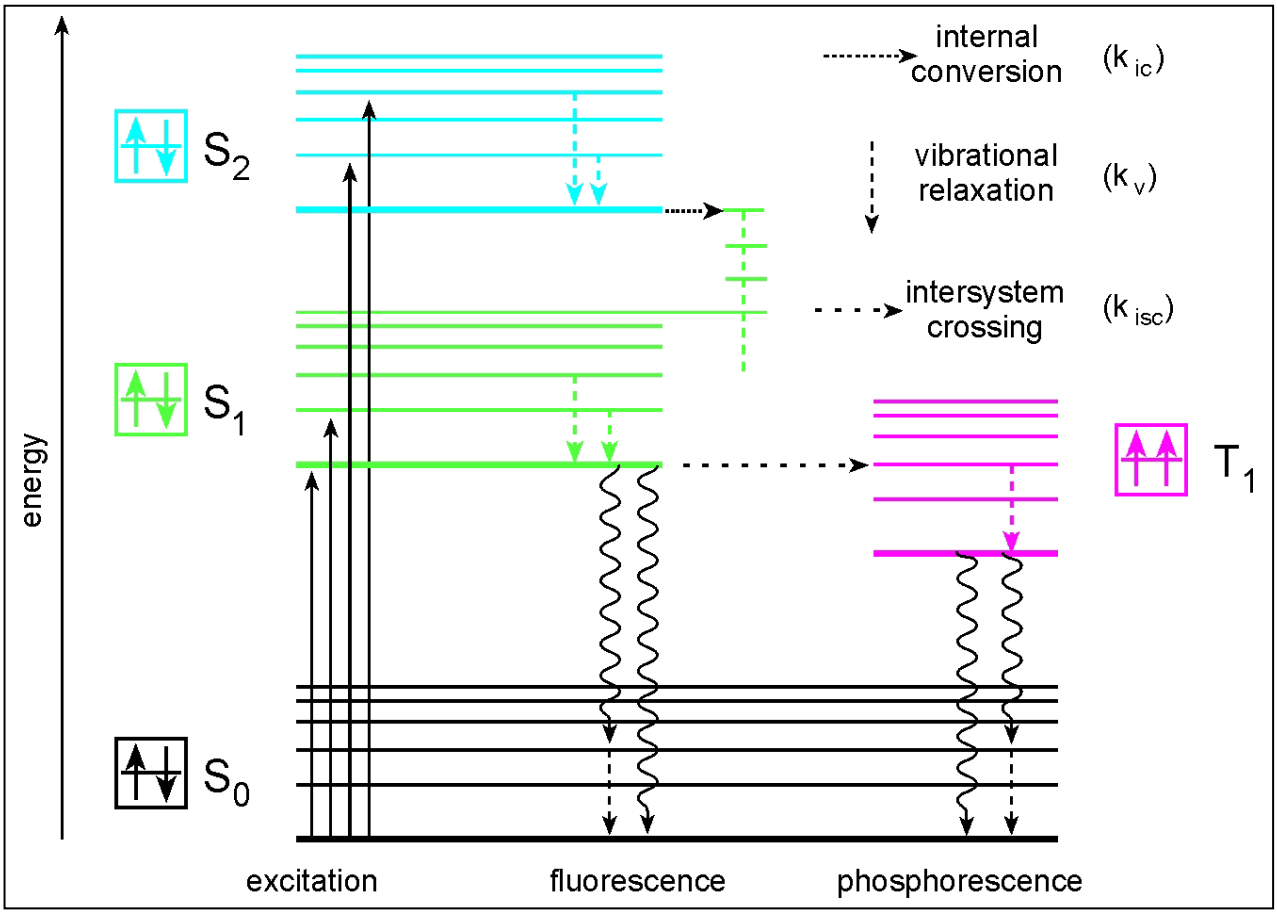


Turning the moving mirror by Δx results in enhancement only at wavelengths which are integral multiples of the path length: $\Delta x = k\lambda$. Selects a series of wavelengths: **Fourier transformation**

Luminescence spectroscopy

Background:

(See in the Manuel LIGHT EMISSION)



Jablonski-diagram

photon **absorption** within femtoseconds **fs** (10^{-15} s)

unstable excited state

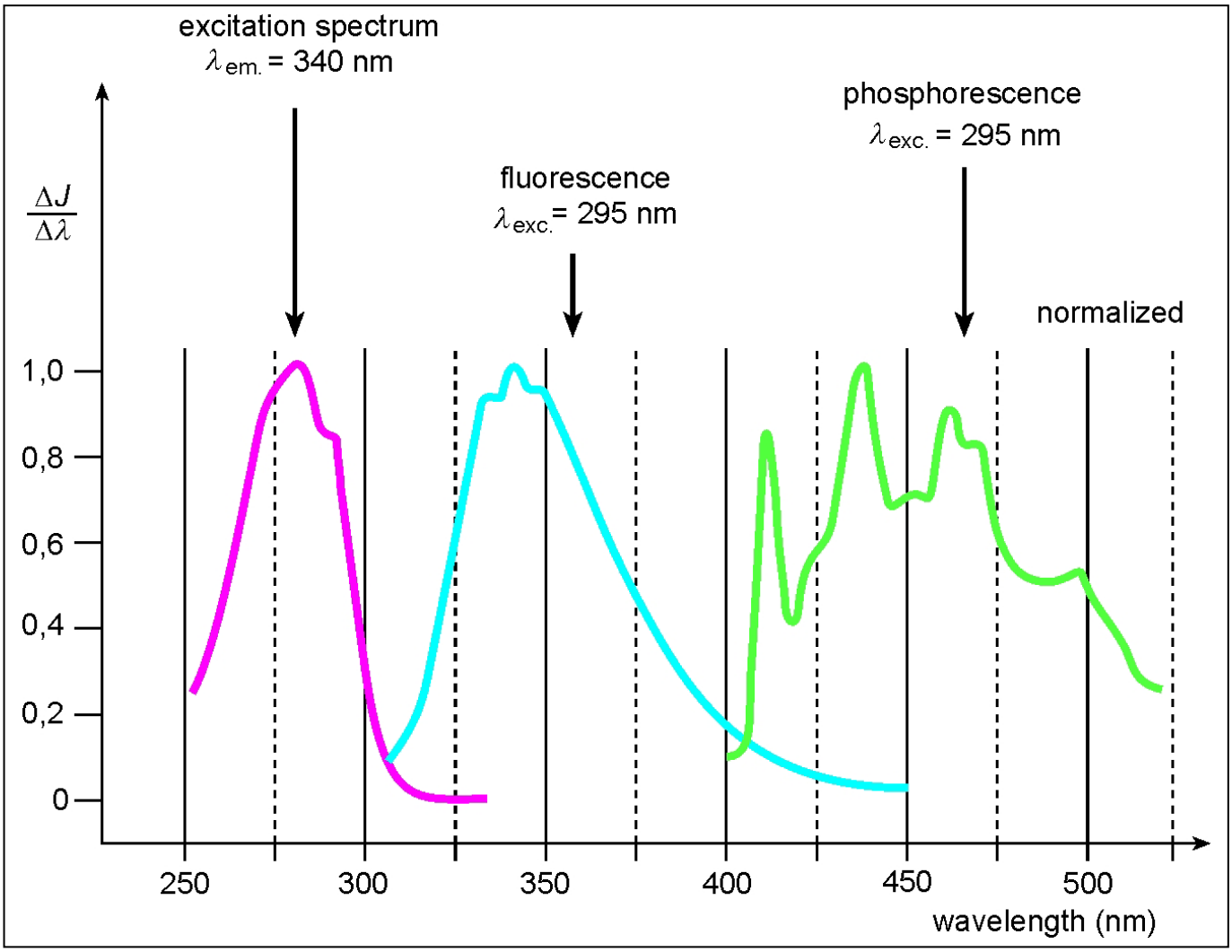
Kasha's rule: the excited molecule reaches the lowest vibrational level of the S_1 state through considerably fast transitions. Photon emission always occurs from this state.

numerous possibilities (with different probabilities) to release the excess energy and return to ground state S_0

decay of **fluorescence** falls in the time range of **ns** (10^{-9} s)
lifetime of **phosphorescence** is much longer: **µs**; **s** (10^{-6}- 10 s).

Characterisation of luminescence

(triptophane)

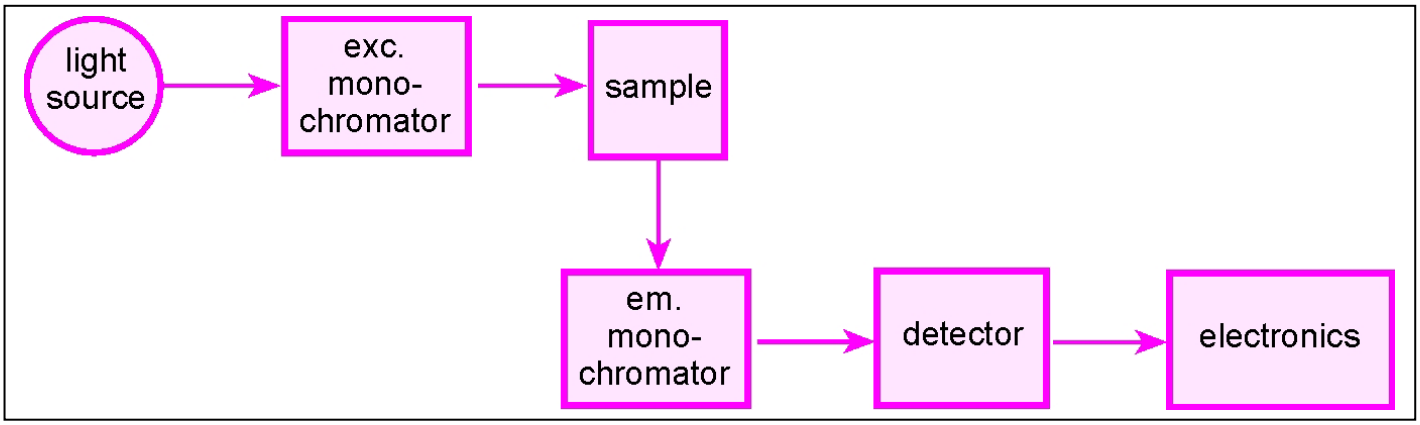


fluorescence spectrum: usually consists of a single band which is less structured and is shifted toward the higher wavelengths with respect to the "absorption" band. This is called as **Stokes-shift**.

phosphorescence spectrum: similar to fluorescence spectrum, it is red shifted with respect to fluorescence band.

excitation spectrum: detection takes place at a fixed emission wavelength and intensity is measured as a function of excitation wavelength.
Thereby the **absorption spectrum** of a selected component with luminescent properties can be selectively determined from a sample containing multiple components.

Blockdiagram of "stady state" spectrofluorimeter



Quantum yield of fluorescence (Q_f):
the quotient of the emitted and the absorbed quanta

$$Q_f = \frac{k_f}{k_f + k_{nr}}$$

where k_f is the probability of emission, k_{nr} is the sum of the reaction rates of non-radiative transitions. The latter involves the probabilities of internal conversion, intersystem crossing, etc.
Quantum yield of phosphorescence (Q_{ph}):

$$Q_{ph} = Q_{isc}\frac{k_{ph}}{k_{ph} + k_{nr,ph}} \quad , \quad Q_{isc} = \frac{k_{ics}}{k_f + k_{nr}} \, .$$

Lifetime of excited state

$$\Delta N = -(k_f + k_{nr})N\Delta t \quad , \quad N = N_0 e^{-(k_f + k_{nr})t} \, .$$

lifetime of fluorescence i.e. the time during which the number of excited molecules decreases to its eth:

$$\tau = \frac{1}{k_f + k_{nr}}$$

Determination of time-dependant fluorescence parameters
Time-correlated one-photon counting

If we employ a short (tipically less than 1 ns) light pulse to excite a sample of fluorophores and measure the time elapsed between the excitation and the arrival of the first photon following the excitation with a detector, then we can plot the frequency of arrival times on a diagram. This diagram coincides with the time-dependence of fluorescence decay.