MODULE V

PHOTOLUMINESCENCE (PL)

Photoluminescence: Light matter interaction

Photoluminescence spectroscopy works in a non- contact mode. It is a non-destructive technique of examining the materials electronic structure.

Basic Principle-

When light strikes a sample,it gets absorbed by impartingits excess energy to the material by thephenomenonknown as photo-excitation. One mannermethod in which sample dissipates this excess energy is through light emission,i.e., luminescence. In case of photo-excitation, luminescence is known asphotoluminescence.

Excitation causes material'selectrons to occupy theallowed excited states. These excited electrons return to their stable, i.e., equilibrium or ground state by dissipatingthe extra energy in the form of either light known as radiative process orby any non-radiative process. The emitted light energy (photoluminescence) is linked with the energy difference in energy of the two electronic states taking part in the transitionbetween the excited and equilibrium states. Whereas the portion of radiative process decides the quantity of the light emitted.

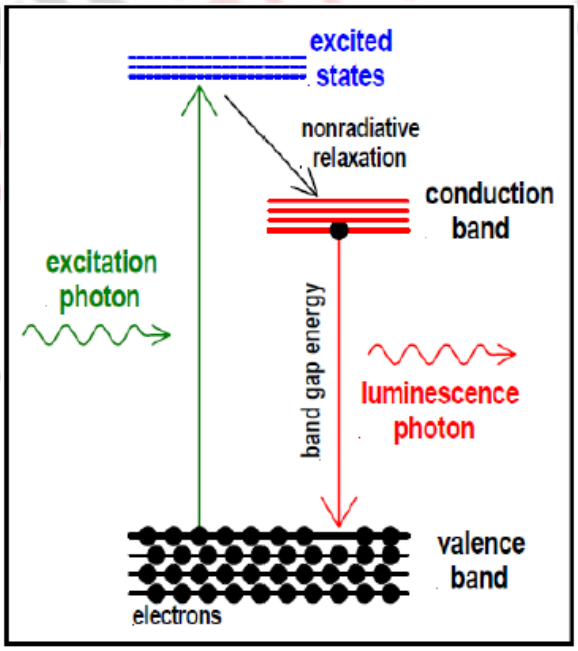


Figure 1 Principle of photoluminescence spectroscopy (PL).

Photoluminescence (PL) Significance-

In PL systems, theaggregation of chromophore commonlycauses quenching of light emission due to aggregation caused quenching (ACQ). This implies that it is essential to utilize and study fluorophores in diluted conditionsor as isolated molecules. This causes poor sensitivity of devices using fluorescence, such as biosensors and bioassays. In light emitting process, some examples have been described in

therecent times about luminogen aggregation where it has played a constructive role instead of the destructive role. With respect to the solid-state device a process known as aggregation-induced emission (AIE) is of huge potential importance.Fluorophore lumniscent properties can be examined by the technique known as photoluminescence spectroscopy.

Photoluminescence different modes-

- **Resonant radiation:**In this process, a specific wavelength photon gets absorbed with the immediate emission of equivalent photon. This process does not involve any appreciable internal energy transitions between absorption and emission, further the time scales of the process is of the order of 10 nanoseconds.

- **Fluorescence:** The chemical substrate, when it is undergoing the internal energy transition by emitting photon before returning to its ground state, certain joule of absorbed energy getsliberatedsuch that the emitted light has lower energy in comparison to the absorbed. Fluorescence is the one of the known mechanism whose(short) lifetime is about 10^{-8} to 10^{-4} s.

- **Phosphorescence:** It is a radiation based transition, wherein the absorbed energy experienceselectronic transition having different spin states, i.e.,intersystem crossing (ISC). Phosphorescence phenomena lifespan is typically from 10^{-4} - 10^{-2} s which is considerablylengthierin comparison to Fluorescence lifespan. Thus, phosphorescence phenomena occurrarely when compared to fluorescence, as the molecule in its triplet state has a more chance of experiencingintersystem crossing to lower energy state before the occurrence ofphosphorescence.

Relation between absorption and emission spectrum-

At lower energy, chance of fluorescence and phosphorescence is more than absorption (the energy of excitation). As presentedin **Figure 2**, in case of absorption, $\lambda_0$wavelength means transition from the ground state of vibration i.e. S_0 to S_1. When absorbing radiation, S_1molecule which excited vibrationallygoes to lower vibrational level beforeemitting any radiation. $\lambda_0$wavelengthcorresponds to transition ofvery high energy, cascade of peaks occurat higher wavelength. Both emissionas well as absorption spectrum arelikelyto have mirror image relation if spacing of vibrational levels are approximately equivalent and if the probability of transitionare alike.**Figure 3**,λ_0 transitions do not overlap completely. As depicted in **Figure 2**, a radiation absorbing molecule which is primarily in its ground state, S_0; have a firm geometry in addition to solvation. The transitions in the electronic states are rapid in comparison to atoms vibrational movement or the solvent molecules'translational movement, oncethe radiation is absorbed, the S_1excited molecule yethave its geometry as well as solvation S_0state. Geometry in addition to solvation is modified to an utmost appropriate amount soon after the excitation. This rearrangement lowers the energy of excited molecule. When an S_1 molecule fluoresces, it returns back to the S_0 state having S_1 geometry and solvation. This unbalancedarrangement must have a higher energy than that of an S_0 molecule having S_0 geometry and solvation. The net outcome has been shown in **Figure 2** in which excitation energy is higher than the emission energy.

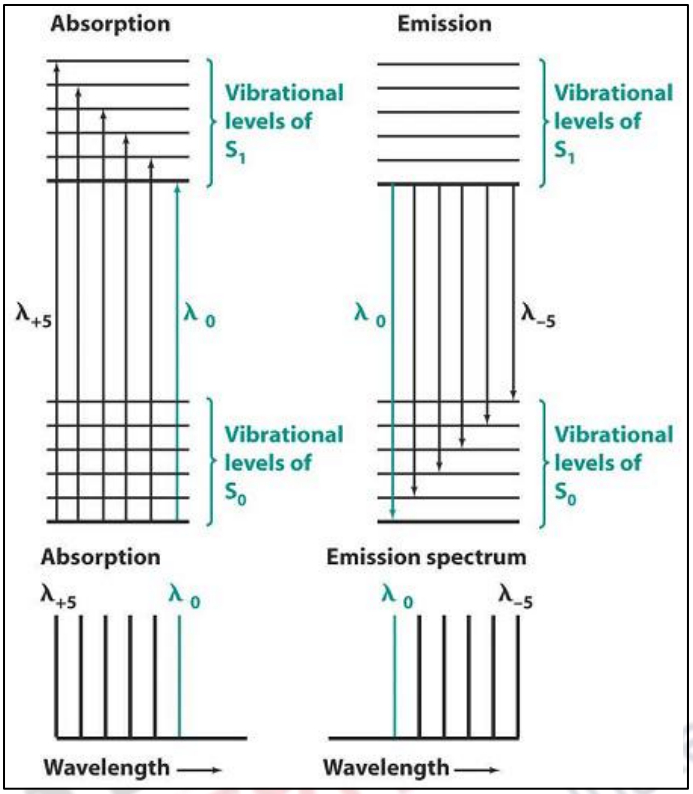


Figure 2Figure representing the energy-level diagramswhich mentions that why structure is seen in the absorption as well as emission spectrumalso why the spectra are roughly mirror images of each other.

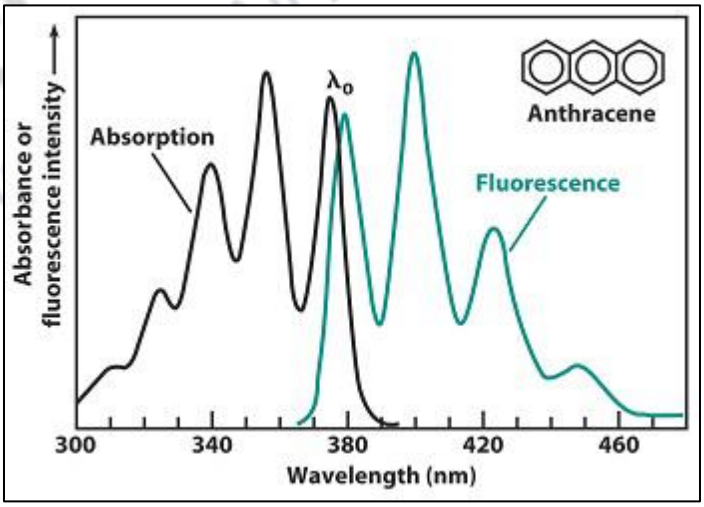


Figure 3Emission as well as excitation spectra of anthracene whichpossesses the identical mirror appearance relation at the absorption and emission spectra.

Instrumentation of photoluminescence-

The fluorescence from a sample is recorded and measured by an analytical device known asspectrofluorometer. Scanning of the excitation, emission or both wavelengths is done in order to record the fluorescence.Throughextraattachments, study of signal deviationwith respect to time, temperature, concentration, polarization, or other variables isobserved. Block diagram of fluorescence spectrometeris represented in **Figure 4**. Fluorescence spectrometers use laser sources, which hasmonochromator (wavelength selectors), laser source(sample illumination), detectors and corrected spectrum.

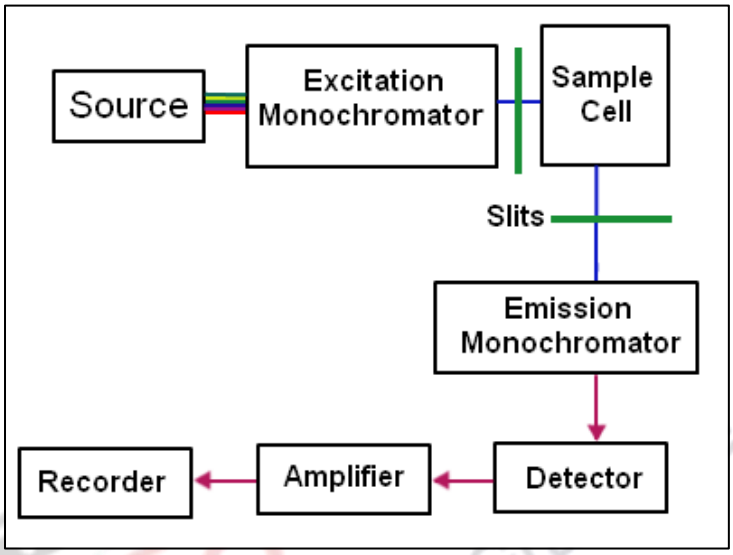


Figure 4Fluorescence spectrometerblock diagram.

- **Source of Illumination:**Thesource of light used is a continuous type, 150 W ozone free xenon arc lamp.Lamps' light is accumulated by a diamond turned elliptical shaped mirror, which isthen focused onto the excitation monochromators'entrance slit. A quartz based window is used to isolate excitation monochromator from the housing of lamp, which vents heat out of the device, and shields against the unlikely occurrence of failure of lamp. Resolution over the complete spectrumstretches and reduces spherical aberrations and re-diffraction.

- **Monochromators:**There are two types of monochromators, i.e.,Excitation and Emission monochromators. Entire reflective optics is used by it in order to keepgreat resolution over the fullrange of spectrumas well asto reduce aberrations (spherical) and re diffraction.

- **Gratings:** Reflection Grating is thecrucial part of a monochromator, whose purpose is to disperse striking (incident) light through grooves which are positioned vertically.Spectraareacquired by gratings rotation which contain 1200 grooves per mm, and are blazed at 330 nm (excitation) at 500 nm (emission). To overcome oxidation of the grating, it is coated with a protechtive layer of MgF_2.

- **Slits:**Very flexible slits are used at the entrance and exit points of the monochromator.Bandpass of the incident light is determined by the slits width on the excitation monochromator whereas fluorescence intensity signal is controlled (recorded by signal detector) by the emission monochromator's slits. When setting slit width, the tradeoff is intensity of signal versus spectral resolution. In a case where slit width is wider, shows decrease in resolution because extra

lightfalls on the sample as well as on the detector whereas when narrower slits are used, higher resolution is obtained but at the cost of signal.

- **Shutters:** Beneath the excitation monochromator's exit slitan excitation shutter is placed and its purpose is toshield sample from photo bleaching or photo degradation bylong exposure to the light. The detector is protected from the bright light through an emission shutter which is positioned just prior to theentrance of the emission monochromator.

- **Sample compartment:**In sample compartment,several optional attachments are present and bundles of fiber optic to take the excitation beam to the sample which is placed remotely and bring back the emission beam to the emission monochromator.

- **Detectors:**There are 2 types of detectors i.e. Signal and reference detector. The signal detector is based on photon counting, which is an R928P photomultiplier tube thatdirects the signal to a photon counting module. The reference detector'spurpose is to monitor the xenon lamp for correctionof wavelength and time dependent output of the lamp. This detector is based on UV which enhances silicon photodiode, placed just prior to the compartment of sample.

Applications-

- **Determination of Band gap:** Band gap represents the energy difference among the conduction band (top) and valence band (bottom) in semiconductors exhibitingradiativetransitions. The range ofPL spectrum of a semiconductor is used for non-destructive analysis of bandgap.Through this mode it is possible to quantify the composition of the element of a semiconductor compound as well as it is cruciallysignificant material specification influencing the device efficacy such as solar cell.

- **Identification of level of Impurity as well as defect:** Some localized defects levels are created when radiative transition occursin semiconductors. Particular defects related to these levels can be recognized by the photoluminescence energy whereas their concentration can be ascertained by the PL amount. The Photoluminescence spectra of the sample atlow temperatures often reveals peaks of the spectra linked with the impurities present inside the material of the host. Highly sensitive fourier transform photoluminescence microspectroscopy have potential forrecognizingverysmall concentrations of intended and unintended impurities whichstronglyinfluencethe quality of material as well asperformance of the device.

- **Recombination phenomena:**Both the radiation and non-radiation based processesinvolve the mechanism known as "recombination" (Return to equilibrium). The emitted PL quantity of a material is straightawaylinkedwith the relative quantity of radiative and nonradiative recombination rates. The quantity of PL and impurities are commonly linked with the nonradiative rates and it is dependent on the photo-excitation level plus temperature which are directly associated to the dominant recombination process. Hence, qualitative PL analysis includes the monitoring of the change in material quality as a function of some conditions like growth as well as processing,which helps in understanding the fundamental physics of the recombination mechanism.

- **Surface structure and excited states:** somebroadlyutilized conventional techniqueslike XRD, IR and Raman spectroscopy are very frequent non- sensitive for catalysts which are oxide supported with less concentrations of metal oxide. PL, on the other hand, is too sensitive to surface effects

or semiconductor based particles adsorbed species therefore, it is utilized as a probe of electron-hole surface processes.

Photoluminescence Spectroscopy limitations-

In spite of the fact that this technique is not qualitative in nature, it can be used to detect low concentration ofoptical centres. The major scientific PL limitation is that several optical centers mightpossessnumerous excited states that are vacant at low temperatures.

Another major limitation of PL is that the luminescent signal gets disappeared. For example, in the PLcharacterization centers of silicon, no sharp-line PL from 969 meV centers were observed when they had captured self-interstitials.

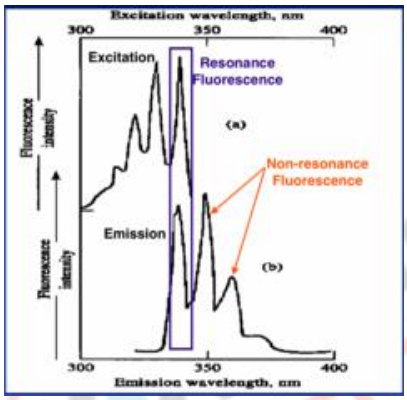
Review your learning:

Long question types:

1) Explain the working principle of PL?
2) Describe other forms of PL?
3) Give applications of PL?

True/False:

1) light emission → What is luminescence?
2) Non-resonance fluorescence → What is the difference between a fluorescence emission spectrum and a fluorescence excitation spectrum?



3) Overlap occurs only for the resonance peak involving transitions between the lowest vibrational level of the ground state and the corresponding level of an excited state. → Why does fluorescence seldom occur from absorbance of UV wavelengths less than 250nm?
4) Photomultipliers
   CCD cameras →What detectors are used with fluorescence spectrophotometers?
5) a singlet-to-triplet transition (or the reverse), which also involves a change in electronic state, is a significantly less probable event than the corresponding singlet-to-singlet transition. →How do transition probabilities differ with singlet and triplet states?

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