Chapter 6

Photoluminescence Spectroscopy

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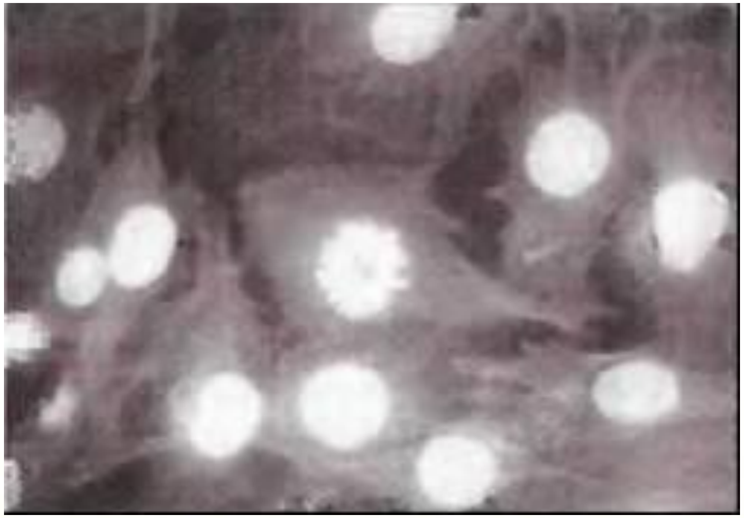
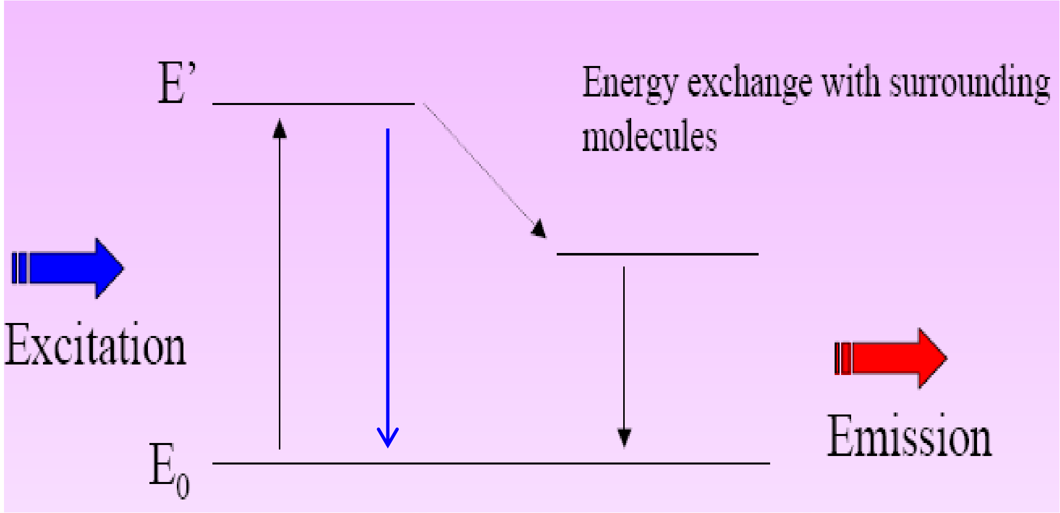
Course Name: Spectroscopy & Materials Analysis

Sib Krishna Ghoshal (PhD)
Advanced Optical Materials Research Group
Physics Department, Faculty of Science, UTM

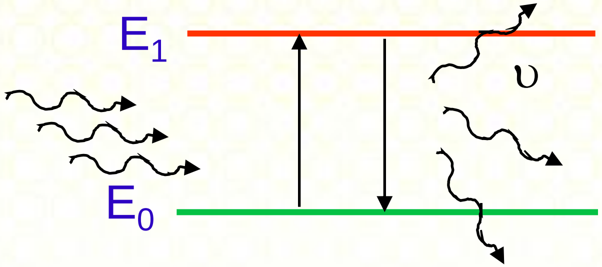
What is Photoluminescence?

Photoluminescence (PL) is a process in which the substance absorbs photons (EM radiation) and then re-radiates photons.





Presentation Outline



- ✓ What is Photoluminescence?
- ✓ Basic Physics of luminescence
- ✓ Principle of PL
- ✓ How PL spectroscopy is performed?
- ✓ What information it captures?
- ✓ Examples
- ✓ Applications
- ✓ Conclusion

Very powerful tool for low dimensional systems, especially for semiconductors!!

Finding right solar material and up-converted lasing material is challenging!!

Definition of Luminescence

✓A material that emits light is called luminescent material.

✓Greek word phosphor (light bearer) is usually used to describe luminescent nature.

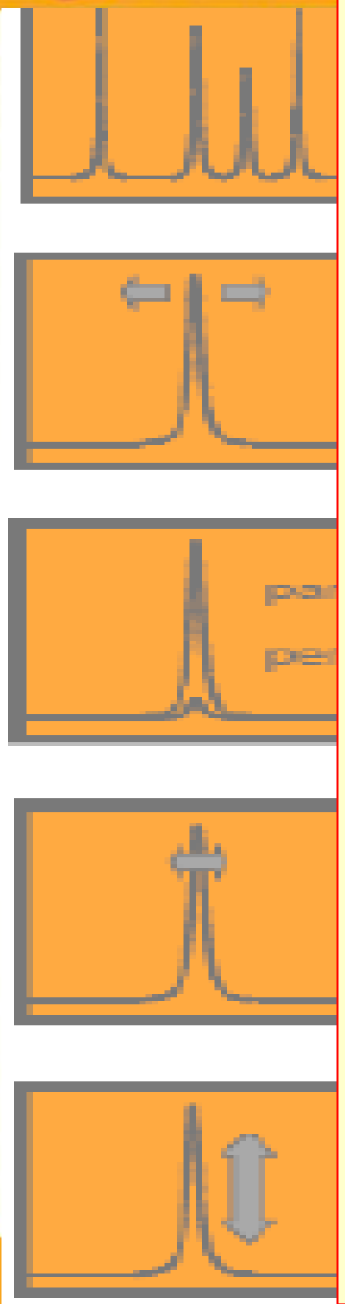
✓ It emits energy from an excited electronic state as light.

✓ Some of the incident energy is absorbed and re-emitted as light of a longer wavelength (Stoke's law).

✓ The wavelength of the emitted light is characteristic of the luminescent substance and not of the incident radiation.

✓ The emitted light carries the materials signature.

Analyses of Samples Fingerprints Captured by PL Spectra



Characteristics PL frequencies	**Composition**
Changes in Frequency of PL peaks	**Stress/Strain State**
Polarization of PL peak	**Symmetry/ Orientation**
Width of PL peak	**Quality**
Intensity of PL peak	**Amount**

- ✓ Number of peaks
- ✓ Peak Intensities
- ✓ Peak position
- ✓ FWHM
- ✓ Peak shape

One broad peak may be superposition of two or several peaks: De-convolution is needed

Perkin Elmer LS 55 Luminescence Spectrometer

✓ It operates from 200 nm to 900 nm wavelength.
✓ Below 200 nm it needs vaccum because air can absorb much UV light.
✓ UTM machine does not cover the time and field dependent fluorescence decay.

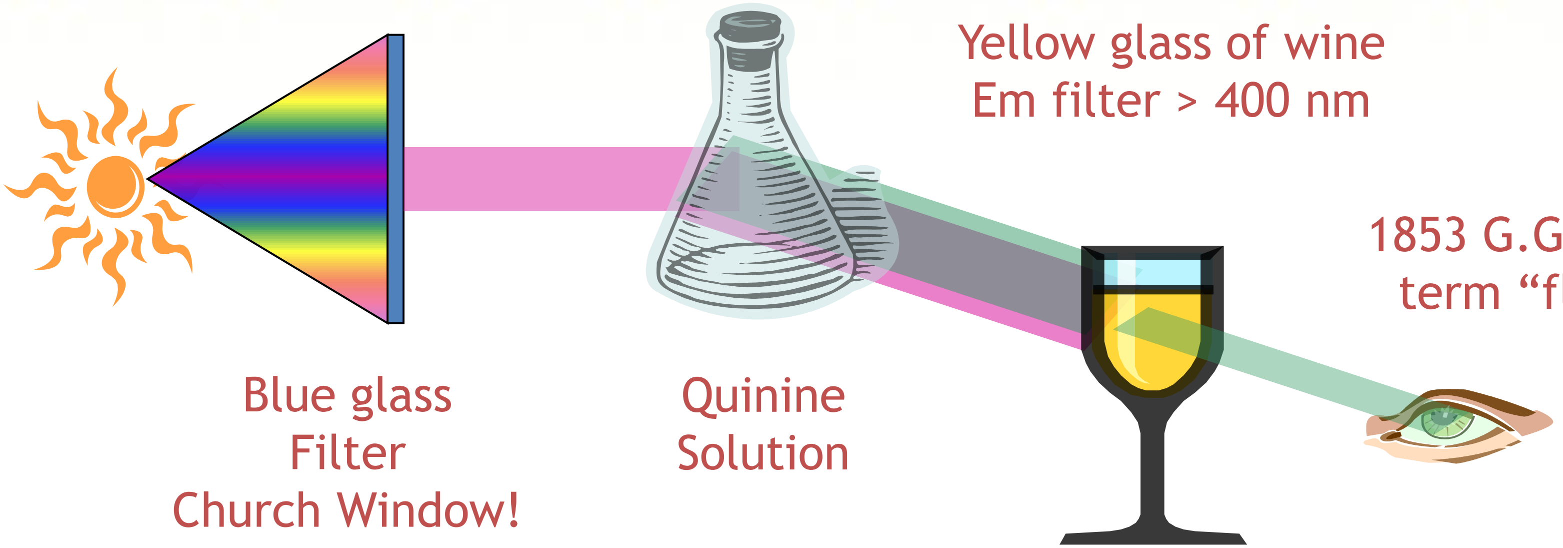
- ✓ Photoluminescence implies both Fluorescence and Phosphorescence.
- ✓One broad peak may be superposition of two or several peaks: De-convolution is needed.
- ✓ Main peak may accompanied with kinks, shoulder or satellites.

Fluorescence – ground state to *singlet* state and back.

Phosphorescence - ground state to *triplet* state and back.

Fluorescence: A Type of Light Emission

- First observed from quinine by Sir J. F. W. Herschel in 1845



Yellow glass of wine
Em filter > 400 nm

1853 G.G. Stoke coined
term “fluorescence”

Blue glass
Filter
Church Window!
<400nm

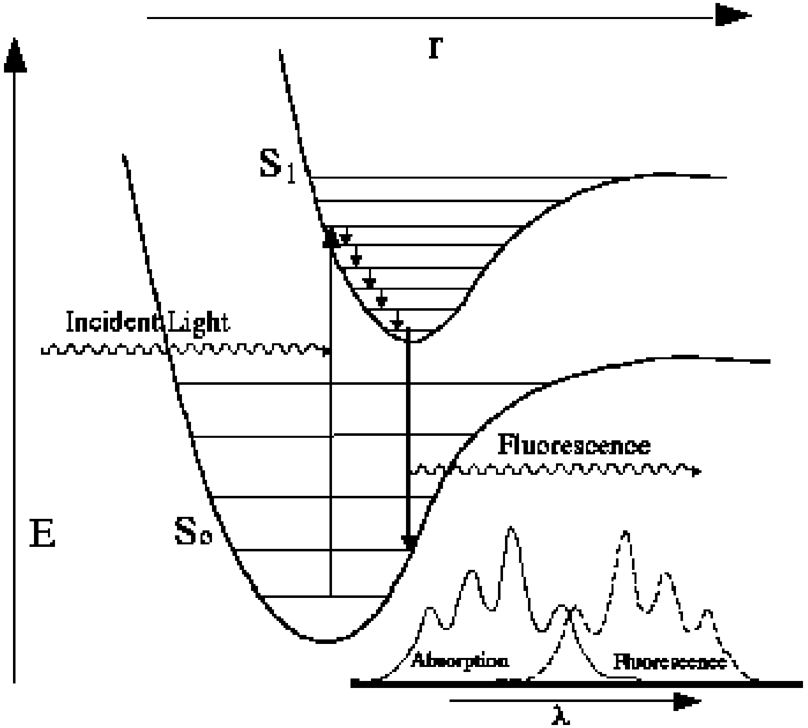
Quinine
Solution

Forms of photoluminescence (luminescence after absorption) are *fluorescence (short lifetime)* and *phosphorescence (long lifetime).*

Common Fluorophores

Typically, Aromatic molecules

- Quinine, ex 350/em 450
- Fluorescein, ex 485/520
- Rhodamine B, ex 550/570
- POPOP, ex 360/em 420
- Coumarin, ex 350/em 450
- Acridine Orange, ex 330/em 500
- Many SC & Low dimensional SC systems
- Some Minerals
- Materials in low dimension
- Glass with Rare Earth Ions



The initial excitation takes place between states of same multiplicity and in accord with the Franck-Condon principle.

Fluorescence ?

What is Fluorescence?

✓ Fluorescence is a photoluminescence process in which atoms or molecules are excited by the absorption of electromagnetic radiation. The excited species then relax to the ground state, giving up their excess energy as photons.

Attractive features

✓ One to three orders of magnitude better than absorption spectroscopy, even single molecules can be detected by fluorescence spectroscopy.

✓ Larger linear concentration range than absorption spectroscopy.

Shortcomings

✓ Much less widely applicable than absorption methods.

✓ More environmental interference effects than absorption methods.

Advantages of Fluorescence Spectroscopy

Highly sensitive technique

✓ 1,000 times more sensitive than UV-visible spectroscopy.

✓ Often used in drug or drug metabolite determinations by HPLC (high performance liquid chromatography) with fluorimetric detector.

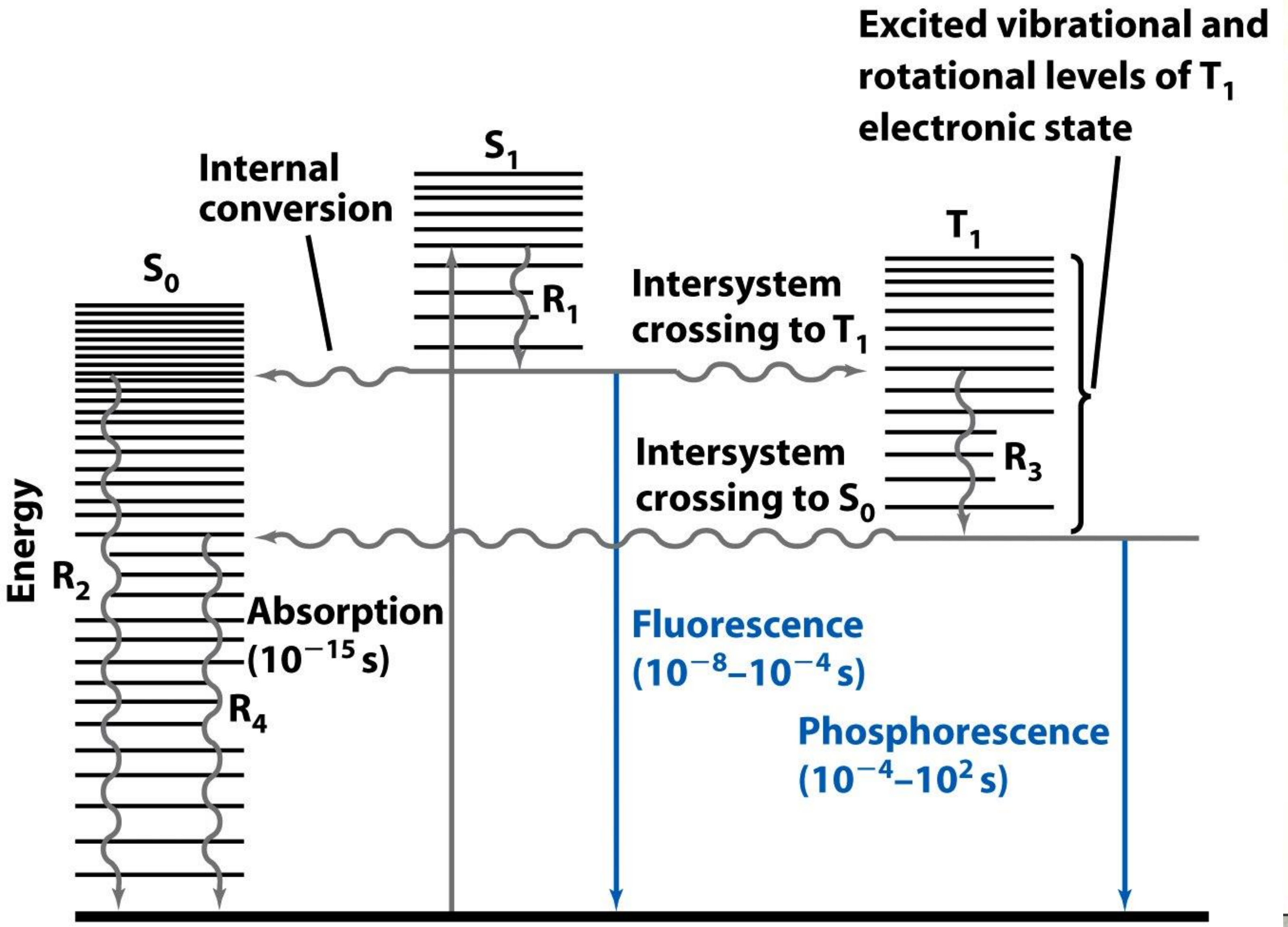
✓ Non-fluorescing compounds can be made fluorescent – derivitisation.

Selective versatile technique

✓ Since excitation and emission wavelengths are utilized, gives selectivity to an assay compared to UV-visible spectroscopy.

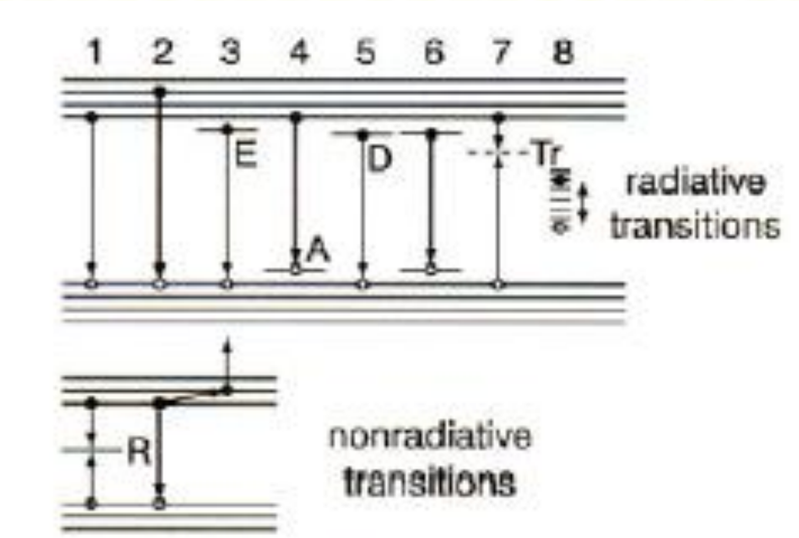
✓ Differing modes of spectroscopy yield wide versatility.

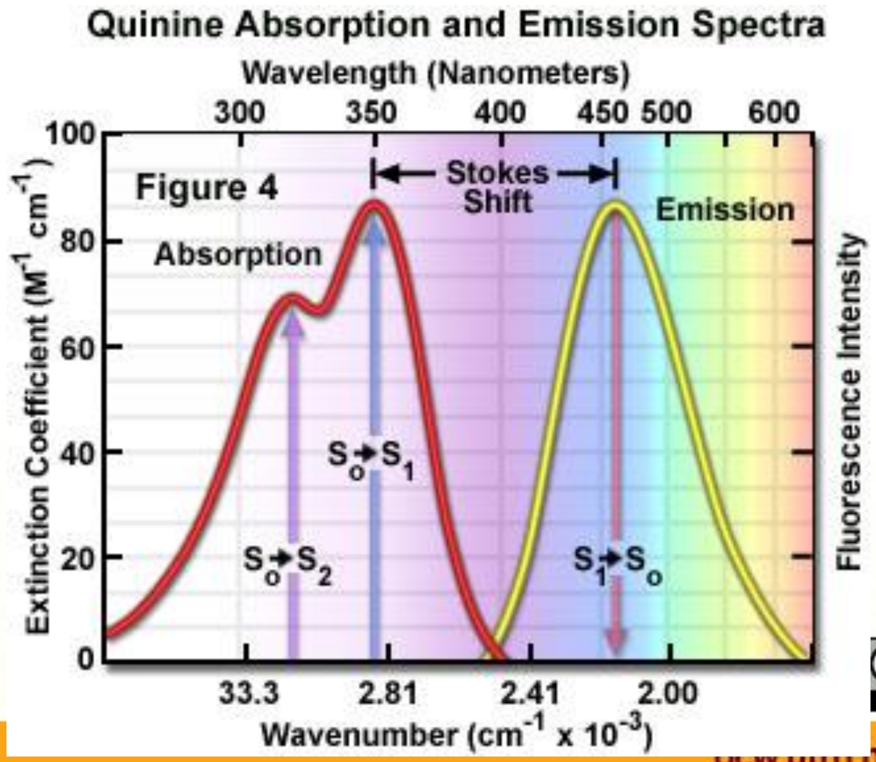
Various Transitions



Luminescence

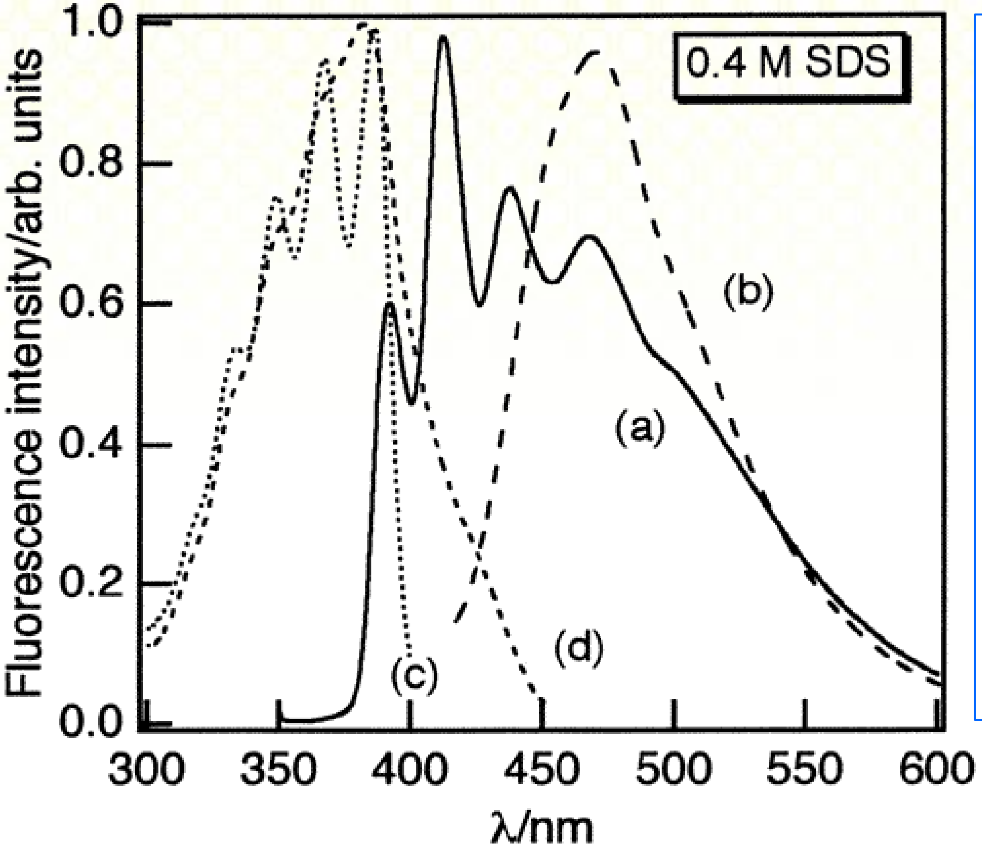
- ✓ "Inverse" of absorption
- ✓ Consequence of radiative recombination of excited electrons
- ✓ Compete with non-radiative recombination processes
- ✓ PL: non-equilibrium obtained by photons
- ✓ Important for Laser, LED and optoelectronics



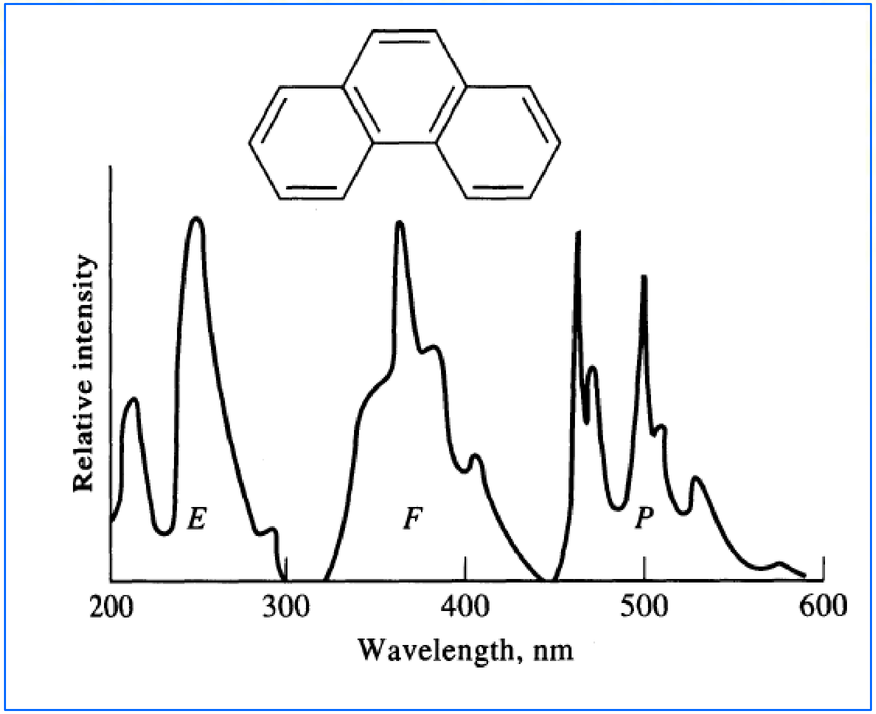


Radiative: Visible photon
Nonradiative: Thermal photon

Typical Fluorescence Spectra



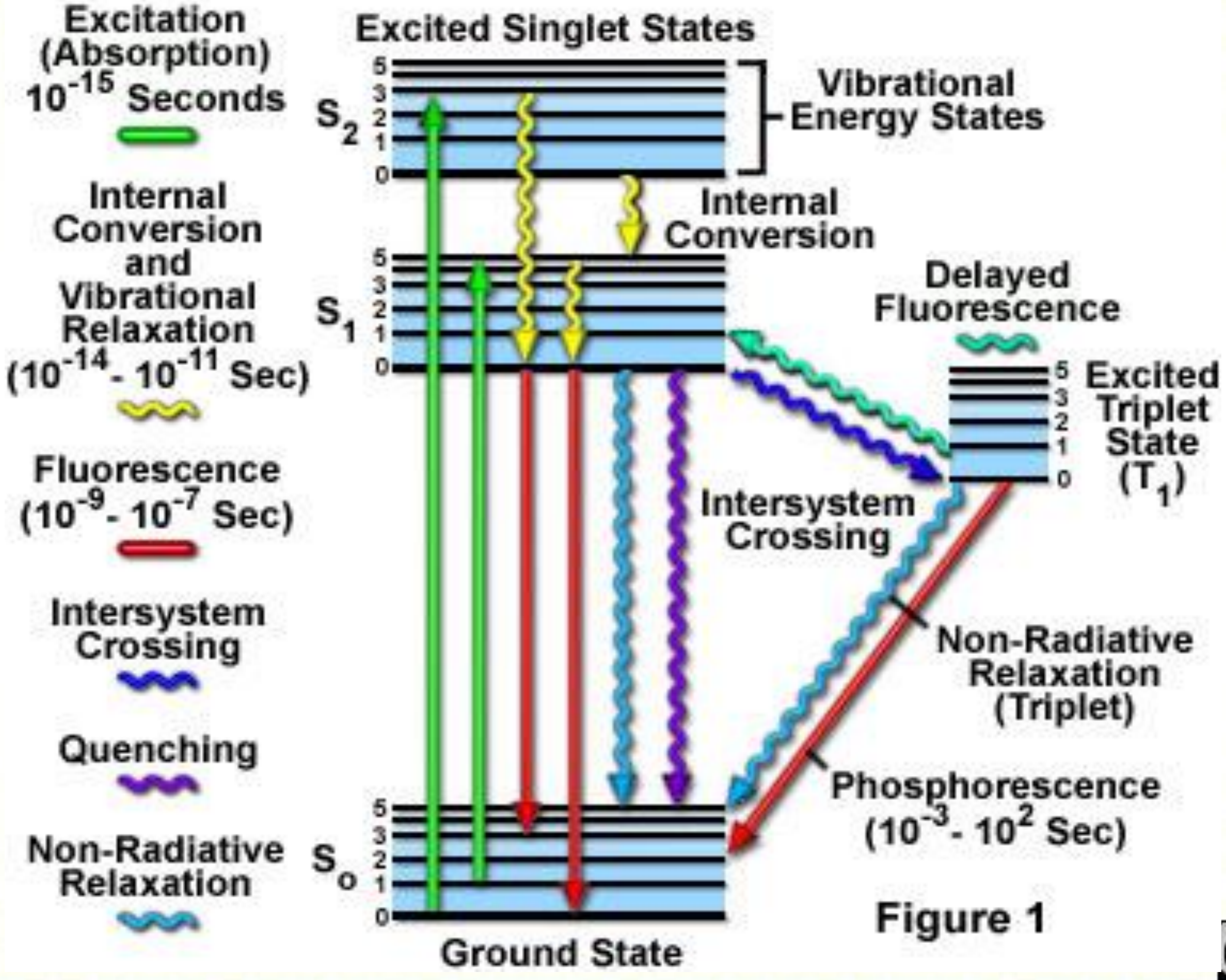
Fluorescence spectra of 9-Anthracenecarboxylic Acid



Fluorescence spectra for 1 ppm anthracene in alcohol

Transitions & Time Scales, Energy Scale…

Jablonski Energy Diagram



Property of Luminescence Spectrum

Fluorescence vs Phosphorescence

- ✓ Phosphorescence is always at longer wavelength compared with fluorescence
- ✓ Phosphorescence is narrower compared with fluorescence
- ✓ Phosphorescence is weaker compared with fluorescence

Why?

Absorption vs Emission

- ✓ absorption is mirrored relative to emission
- ✓ Absorption is always on the shorter wavelength compared to emission
- ✓ Absorption vibrational progression reflects vibrational level in the electronic excited states, while the emission vibrational progression reflects vibrational level in the electronic ground states
- ✓ λ_0 transition of absorption is not overlap with the λ_0 of emission

Why?

Decay Processes

- ✓ ***Internal conversion:*** Movement of electron from one electronic state to another without emission of a photon, e.g. $S_2 \rightarrow S_1$) lasts about 10^{-12} sec.

- ✓ ***Predissociation internal conversion:*** Electron relaxes into a state where energy of that state is high enough to rupture the bond.

- ✓ ***Vibrational relaxation (10^{-10}-10^{-11}sec):*** Energy loss associated with electron movement to lower vibrational state without photon emission.

- ✓ ***Intersystem crossing:*** Conversion from singlet state to a triplet state. e.g. S_1 to T_1
- ✓ ***External conversion:*** A nonradiative process in which energy of an excited state is given to another molecule (e.g. solvent or other solute molecules). Related to the collisional frequency of excited species with other molecules in the solution. Cooling the solution minimizes this effect.

Quantum Yield: A Measure

Fluorescent Species

All absorbing molecules have the potential to fluoresce, but most compounds do not.

Quantum Yield

$$\varphi = \frac{\text{Number of molecules that fluoresce}}{\text{Total number of excited molecules}}$$

$$or\ \frac{\text{Photons emitted}}{\text{Photons absorbed}}$$

Structure determines the relaxation and fluorescence emission, as well as quantum yield

Line shape analyses are important!!

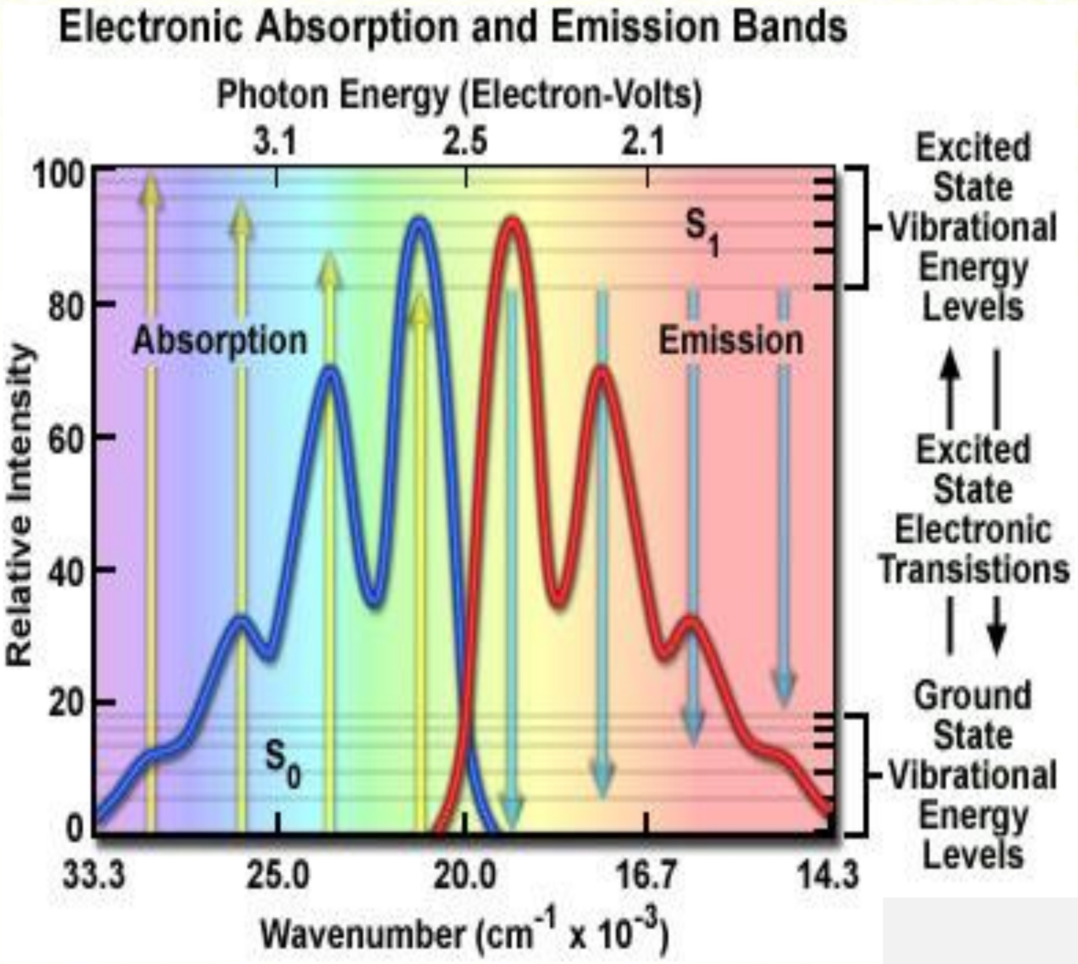
It makes contact with theory, experiment and model!

What is Done in Practice?

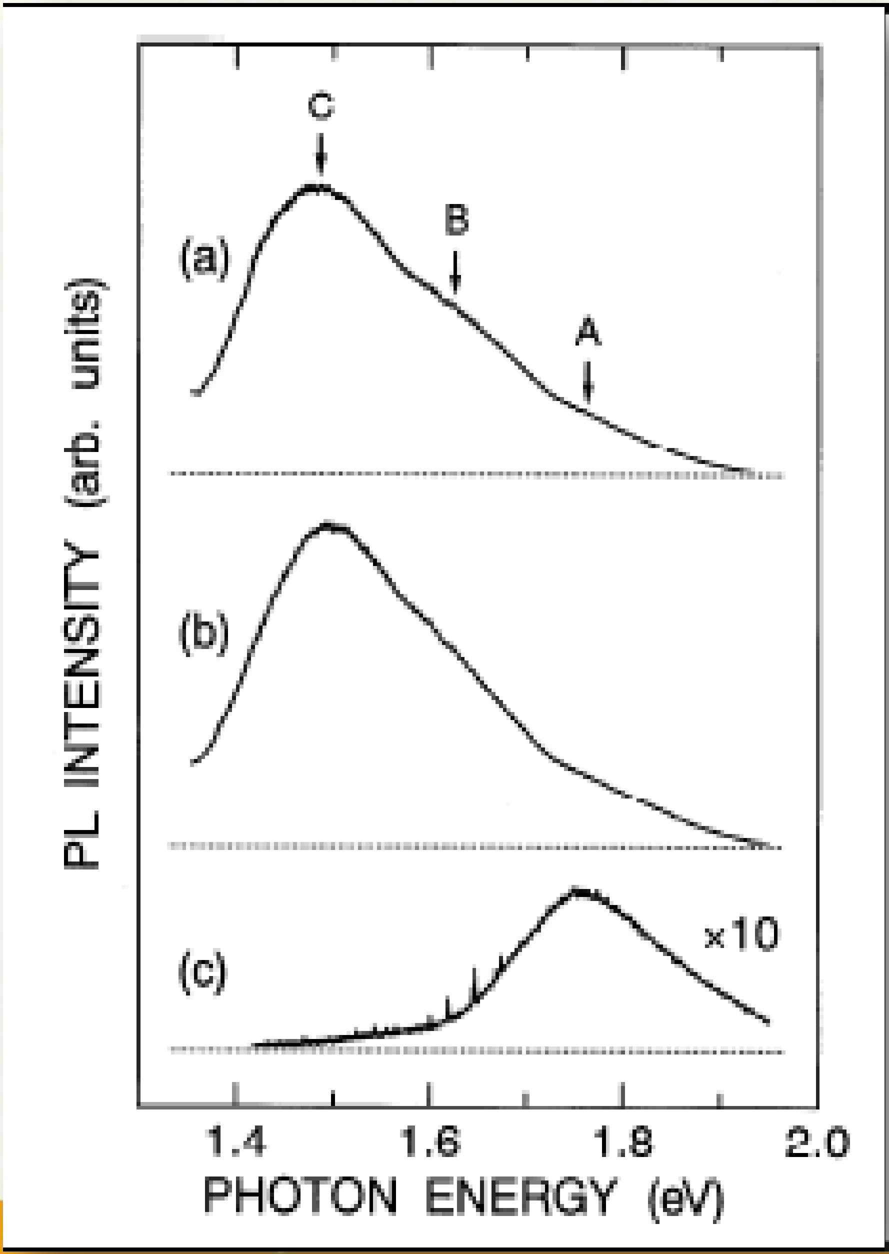
✓ In PL-excitation (PLE) measurements, the PL intensity is recorded as a function of excitation photon energy.

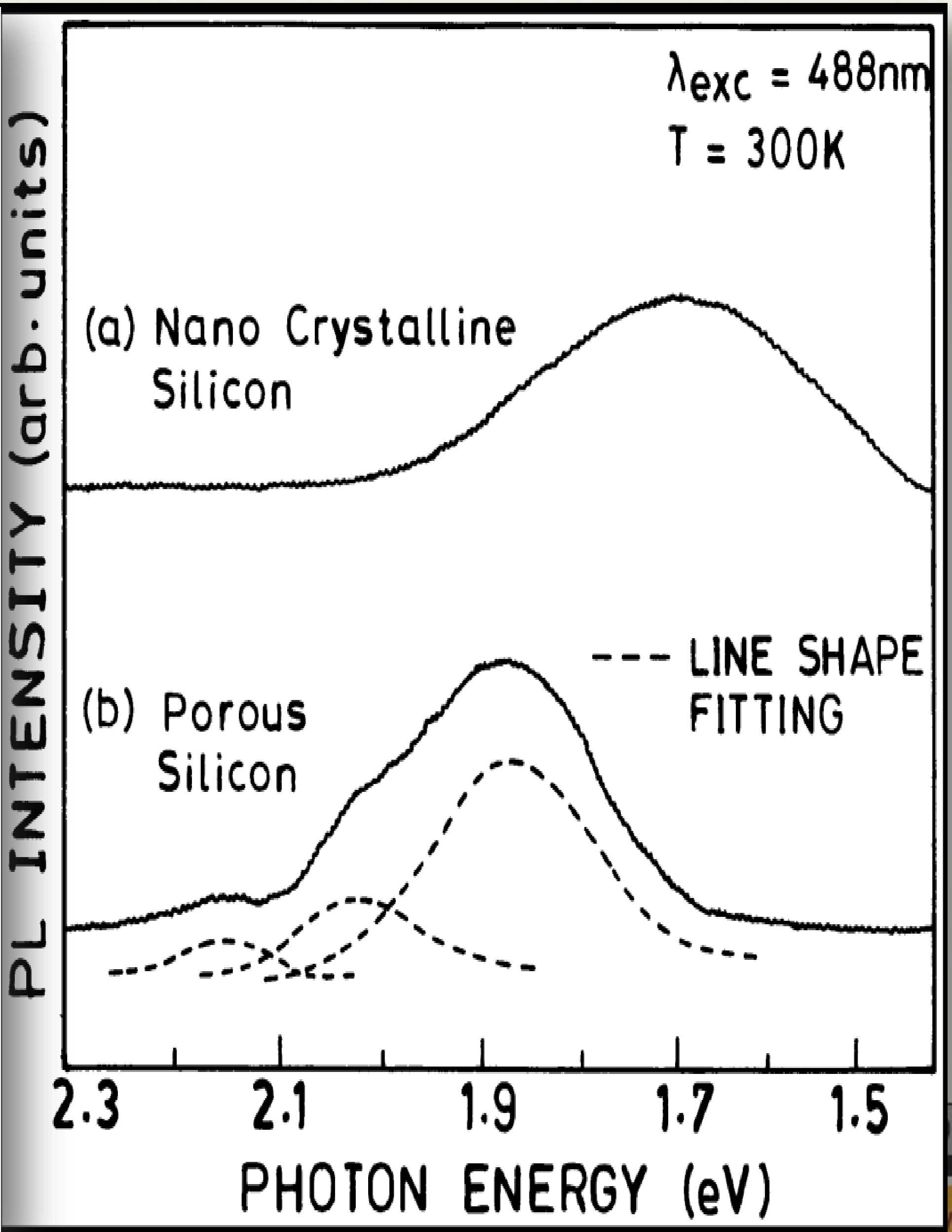
✓ Under a condition of fast intra-band relaxation, PLE is equivalent to linear absorption spectra.

✓ Using micro-PL technique, one can compare the line-shape of PLE with PL at the same microscopic region of 1 mm order.



What is Achieved in Practice?





PL is Used For

✓ Photoluminescence is an important technique for measuring the purity and crystalline quality of semiconductors.

✓ Using Time-resolved photoluminescence (TRPL) one can determine the minority carrier lifetime of semiconductors like GaAs.

✓ Can be used to determine the band gap, exciton life time, exciton energy, bi-exciton, etc. of semiconductor and other functional materials.

✓ Determine the properties, e.g. structure and concentration, of the emitting species.

Photoluminescence

- ✓ **Recombination mechanisms**

The return to equilibrium, also known as "recombination," can involve both radiative and nonradiative processes. The amount of PL emission and its dependence on the level of photo-excitation and temperature are directly related to the dominant recombination process.

- ✓ **Material quality**

Nonradiative processes are associated with localized defect levels. Material quality can be measured by quantifying the amount of radiative recombination.

PL recombination is disadvantageous for Solar Cell Material!!

Variables That Affect Fluorescence and Phosphorescence

- ✓ Both molecular structure and chemical environment influence whether a substance will or will not luminesce. These factors also determine the intensity of luminescence emission.

- ✓ Quantum Yield
- ✓ Transition Types in Fluorescence
- ✓ Quantum Efficiency and Transition Type
- ✓ Fluorescence and Structure

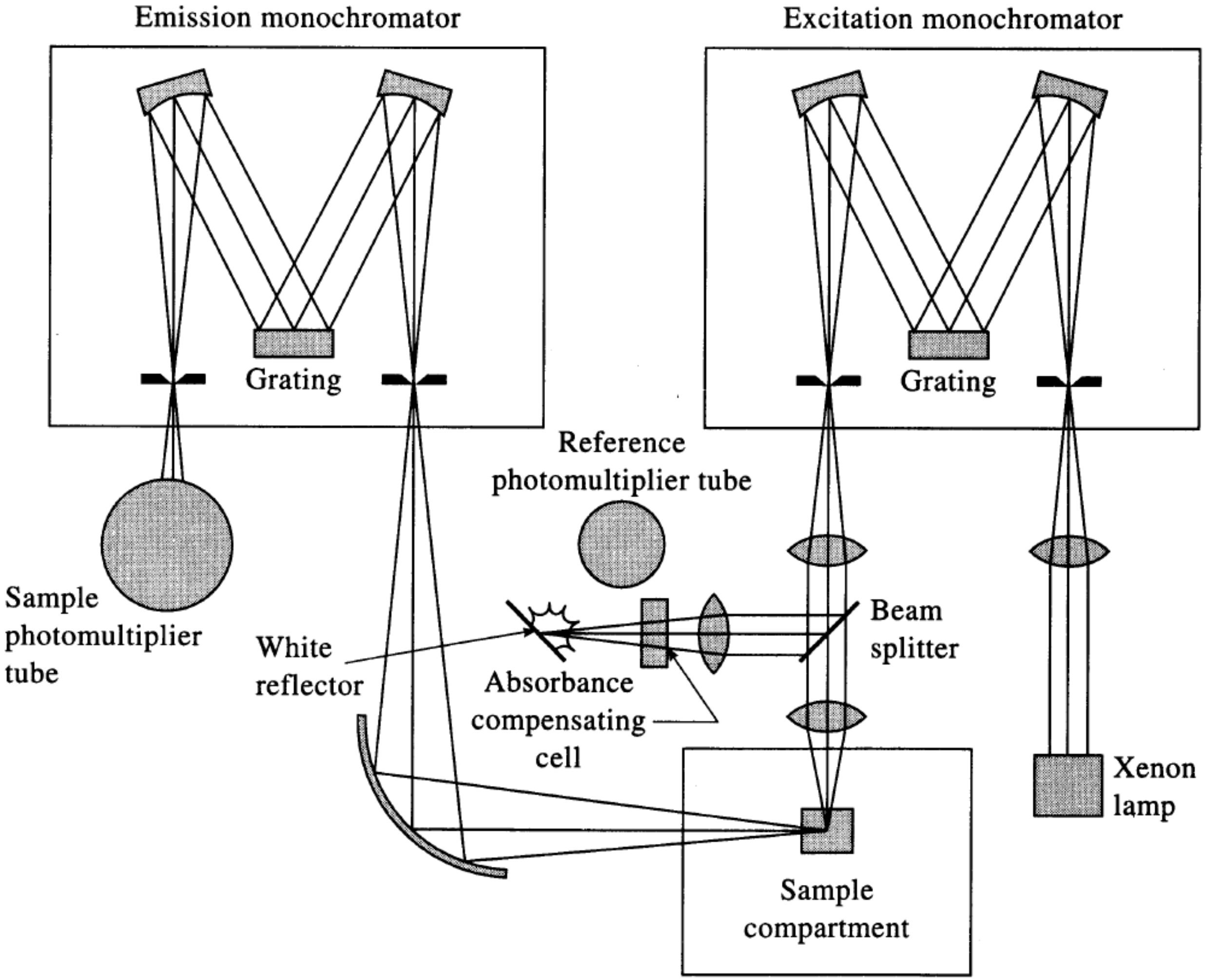
Fluorescence Instrumentation

Major components for fluorescence instrument

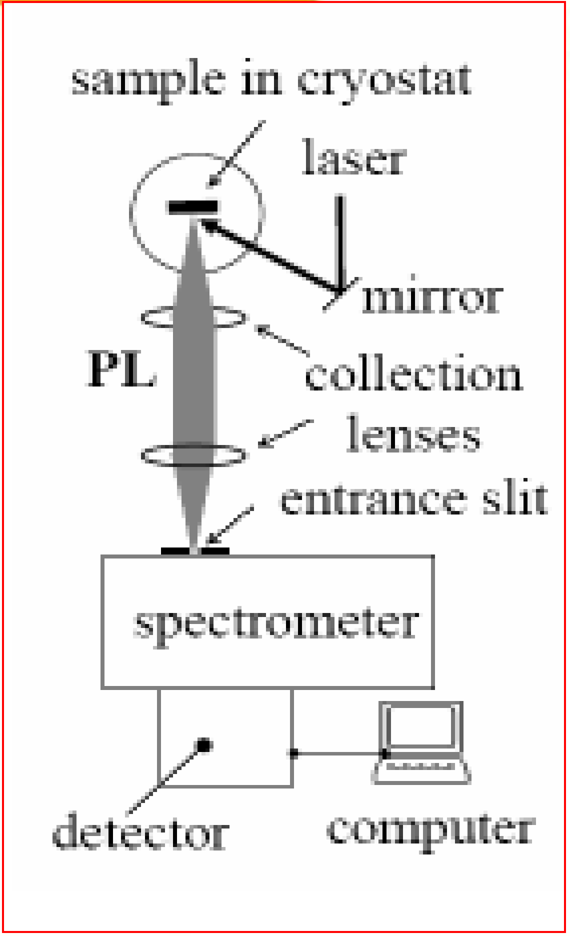
- Illumination source
  - Broadband (Xe lamp)
  - Monochromatic (LED, laser)
- Light delivery to sample
  - Lenses/mirrors
  - Optical fibers
- Wavelength separation (potentially for both excitation and emission)
  - Monochromator
  - Spectrograph
- Detector
  - PMT
  - CCD camera

Instrumentation

Spectrofluorometer - two monochromators for excitation or fluorescence scanning



Types of Photoluminescence Spectroscopy



PL Spectroscopy
- ✓ Fixed frequency laser
- ✓ Measures spectrum by scanning spectrometer

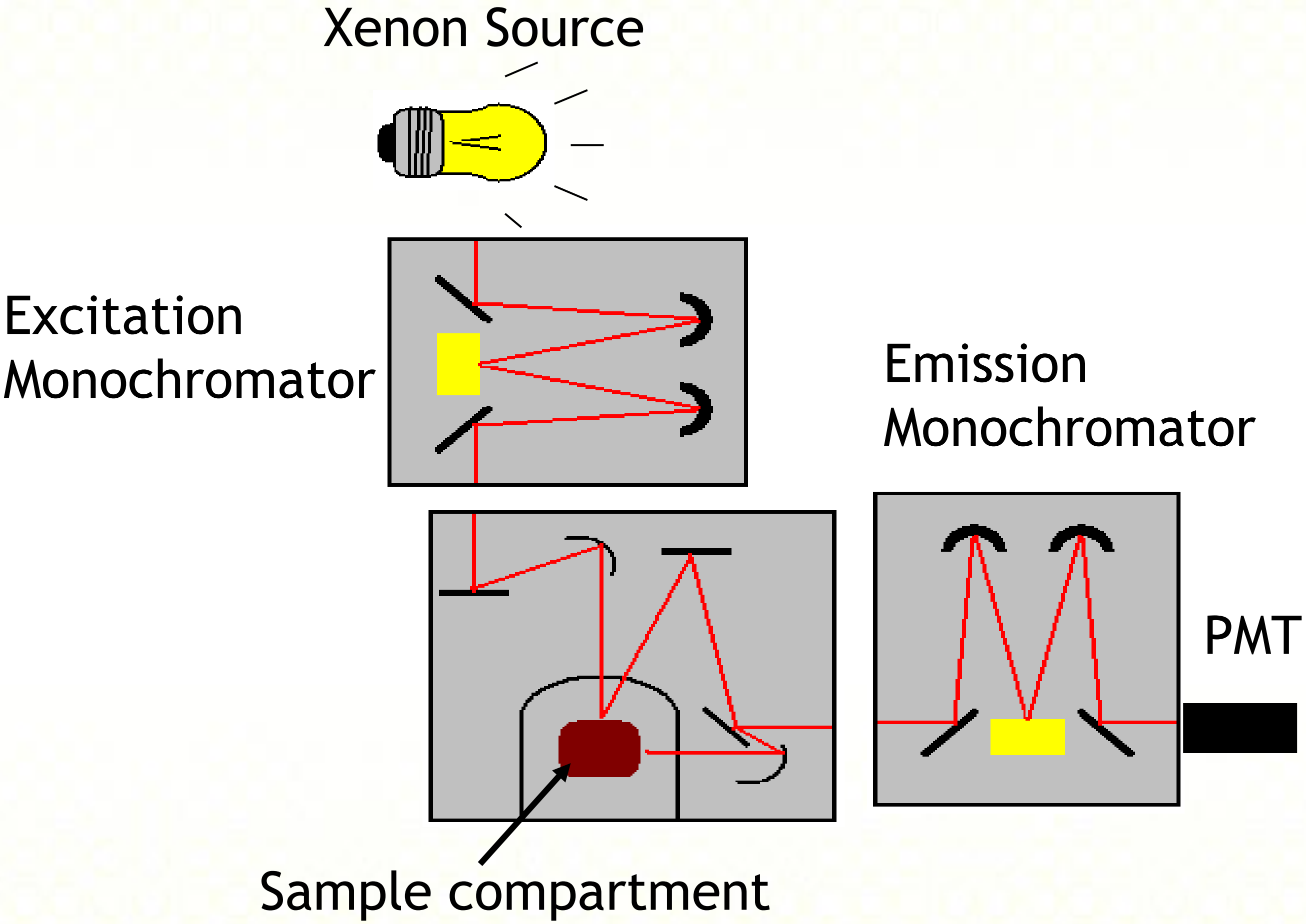
PL Excitation Spectroscopy (PLE)
- ✓ Detect at peak emission by varying frequency
- ✓ Effectively measures absorption

Time-resolved PL Spectroscopy
- ✓ Short pulse laser + fast detector
- ✓ Measures lifetimes and relaxation processes

Needs Tunable Laser Source

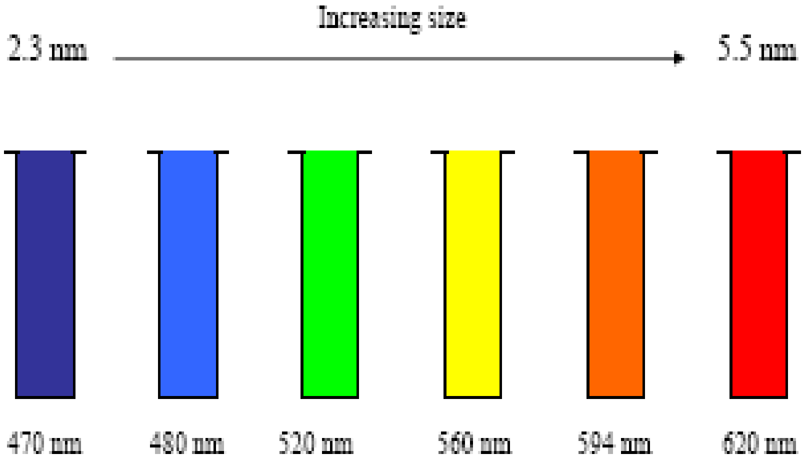
Fluorescence Instrumentation

Spectrofluorometer schematic

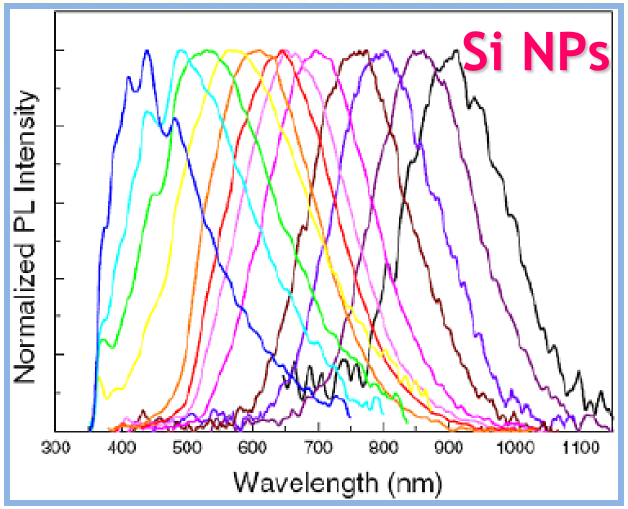


Examples of PL Spectra

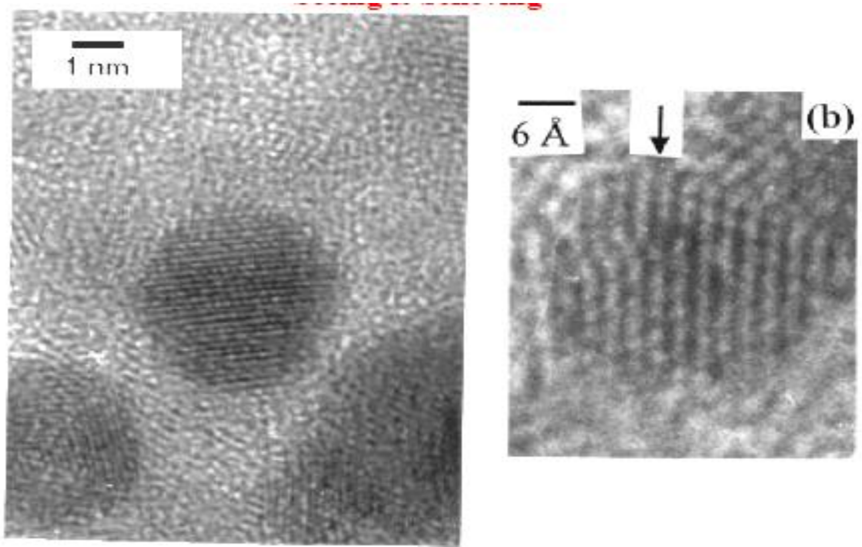
Fluorescence of different size particles of ZnS coated CdSe



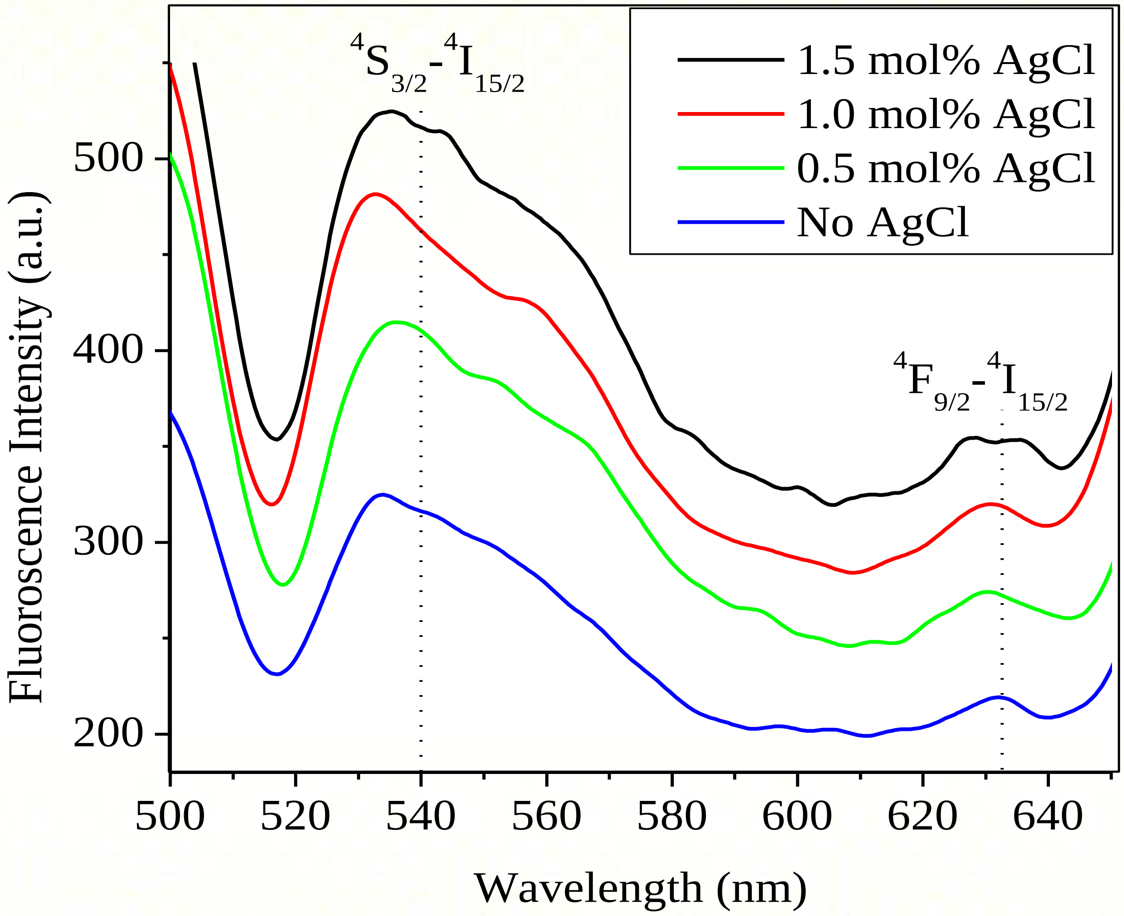
Fluorescence emission wavelength

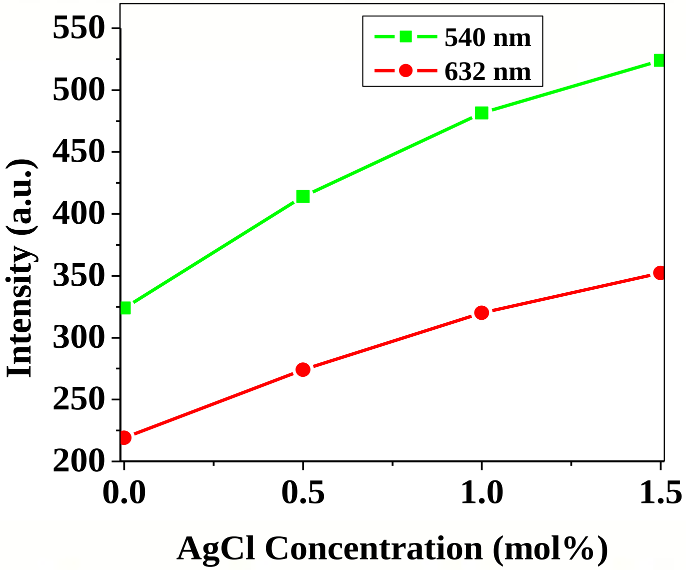


NPs size dependent fluorescence



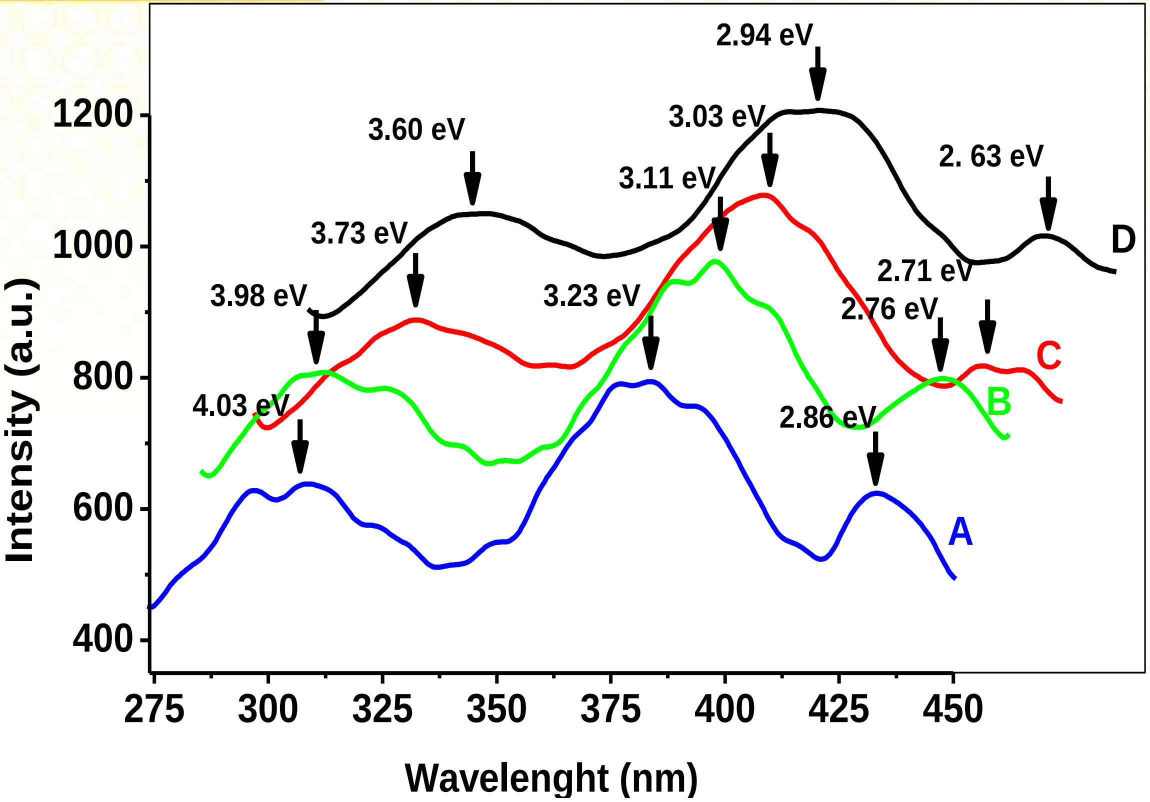
Up-conversion Spectra of Phosphate Glass for Excitation at 797 nm

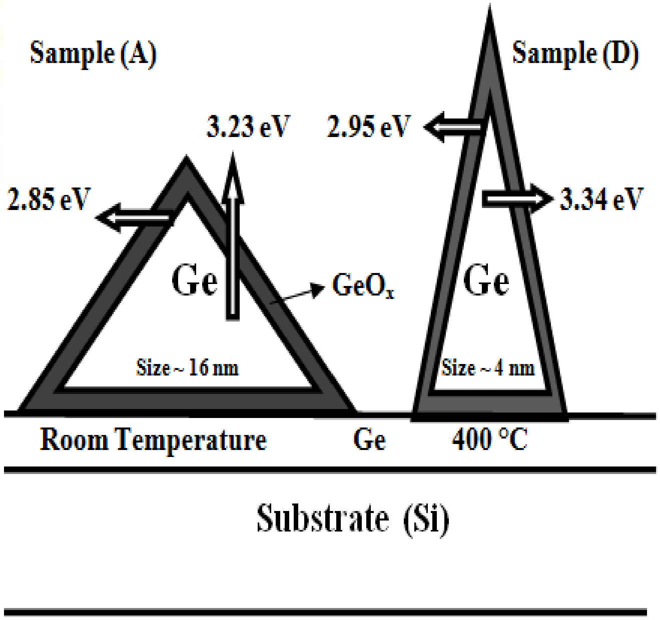




$(59.5\text{-}x)\ P_2O_5+MgO+xAgCl+0.5Er_2O_3$

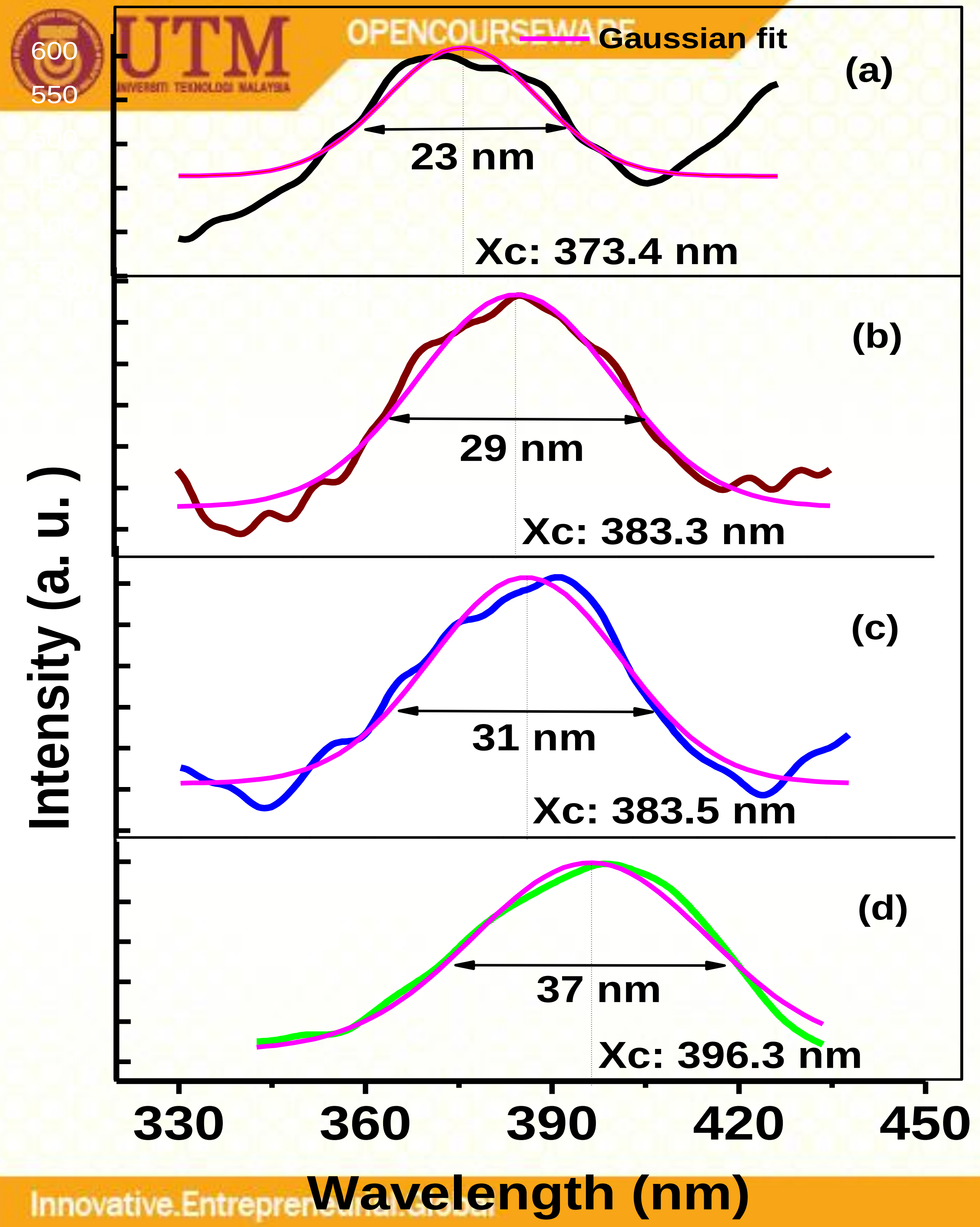
PL Spectra of Ge Nanoparticles





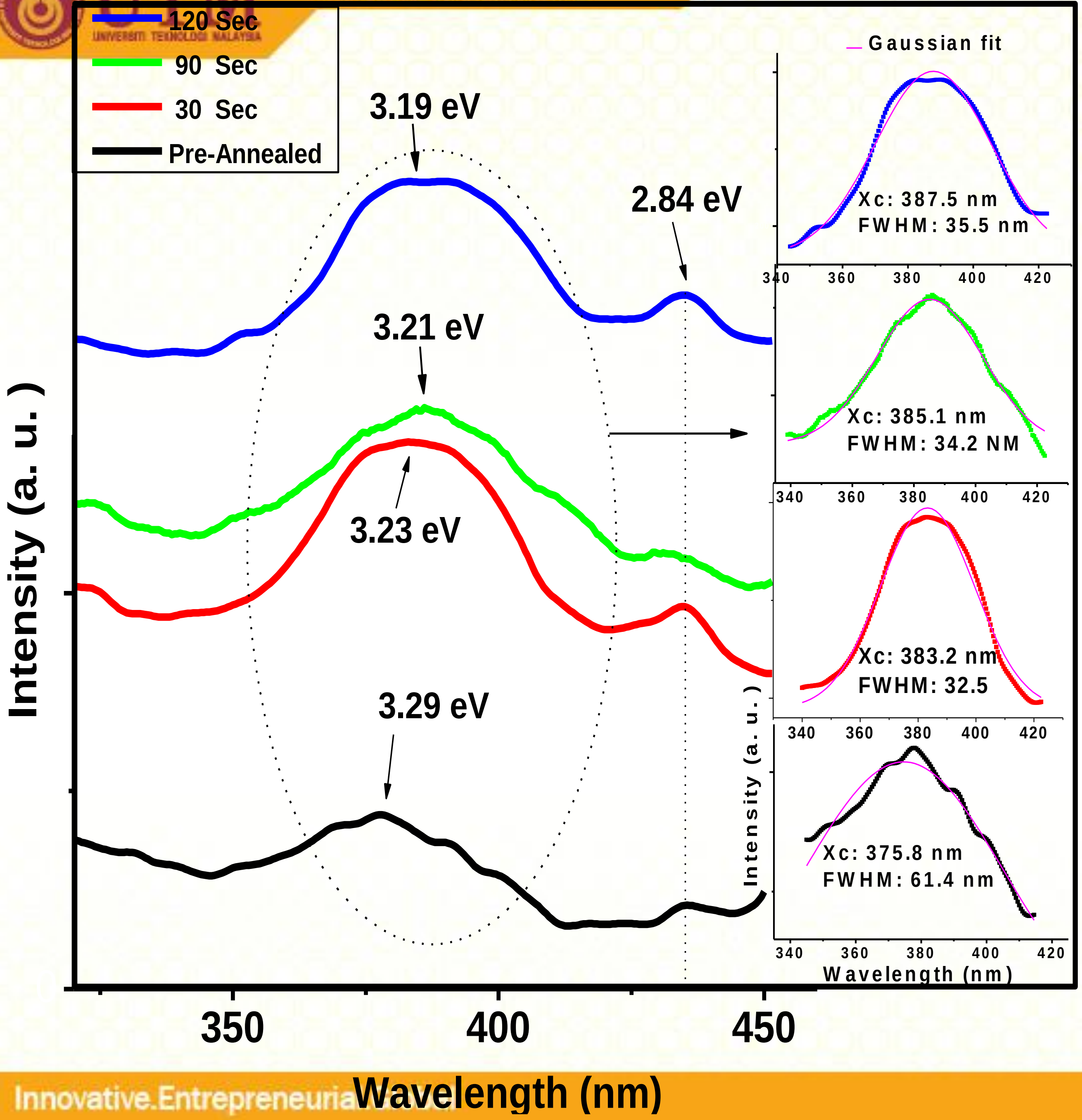
Schematic diagram of S-K growth mode of Ge QDs on Si substrate at two different substrate temperature for sample A (RT), D (400 °C) responsible for the origin of PL peaks presented in fig.

PL Spectra Analyses

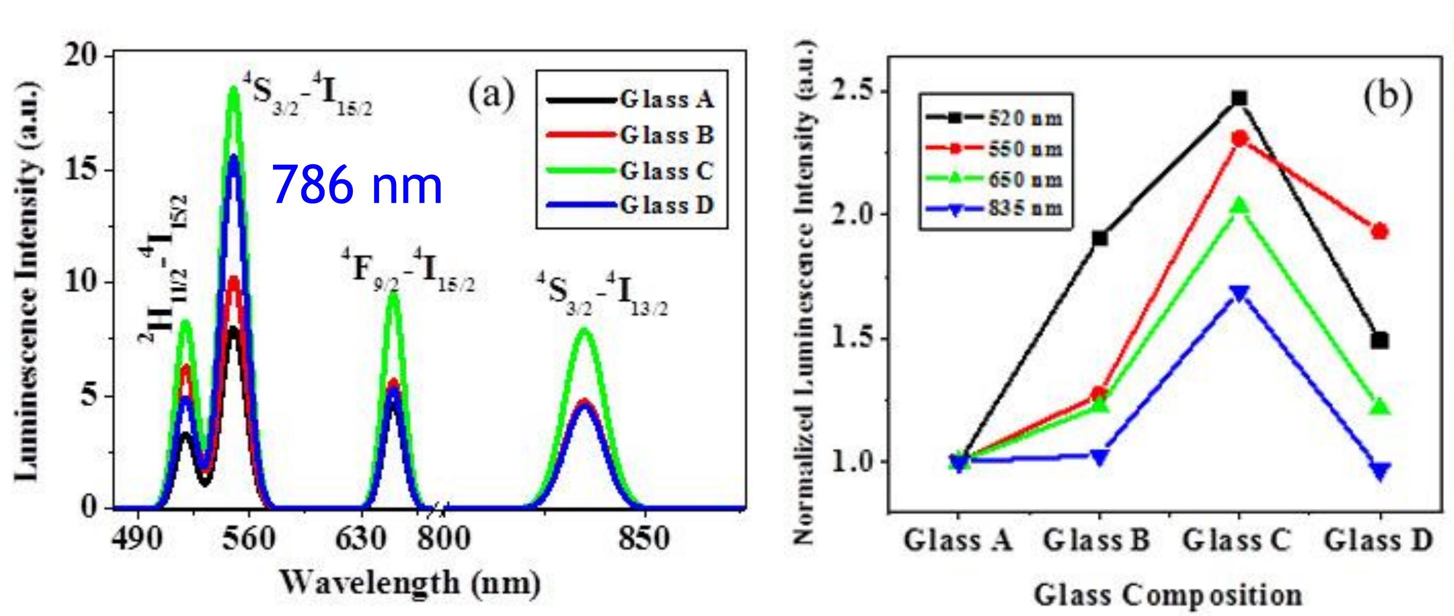


PL spectra of sample A (a), B (b), C (c) and D (d) with the Gaussian de-convolution of intense peak

PL Spectra Analyses



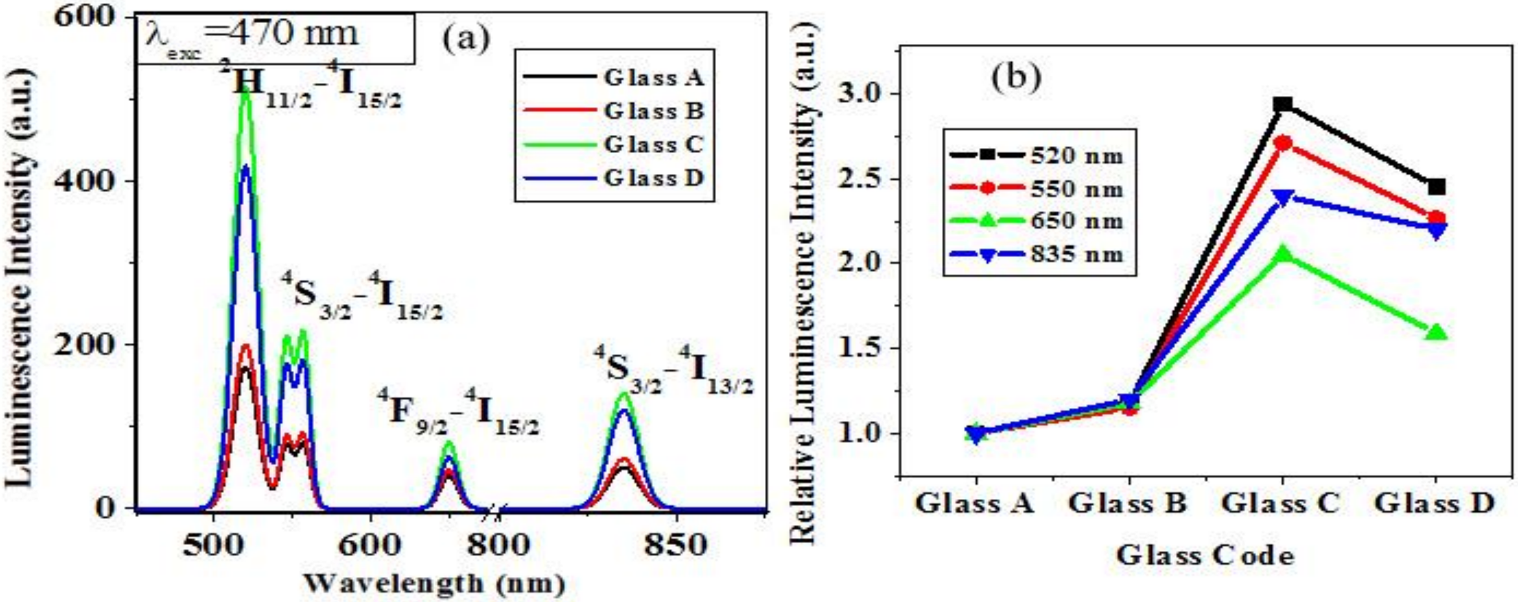
UC PL Spectra



(a) UC Luminescence spectra of glasses under an excitation of 786 nm i) No AgCl, ii) 0.1 mol% AgCl, iii) 0.5 mol% AgCl, iv) 1.0 mol% AgCl (b) Ag concentration dependent emission intensity. Maximum amplification for the green and red bands occur at 0.5 mol% Ag (Glass C).

Four prominent emission bands located at 520 nm, 550 nm, 650 nm and 835 nm attributed to $^2H_{11/2}\rightarrow{}^4I_{15/2}$, $^4S_{3/2}\rightarrow{}^4I_{15/2}$, $^4F_{9/2}\rightarrow{}^4I_{15/2}$ and $^4S_{3/2}\rightarrow{}^4I_{13/2}$ transitions.
(b) All the bands are enhanced significantly by factors of 2.5, 2.3, 2 and 1.7 times, respectively .

DC PL Spectra



(a) Down-conversion luminescence spectra of glasses with i) No AgCl, ii) 0.1 mol% AgCl, iii) 0.5 mol% AgCl, iv) 1.0 mol% AgCl (b) plot of emission intensity vs concentration of Ag (mol%). Maximum amplification for the green and red bands are found to be occur at 0.5 mol% Ag (Glass C).

Applications of PL Spectroscopy

✓ PL spectroscopy is not considered a major structural or qualitative analysis tool, because molecules with subtle structural differences often have similar fluorescence spectra

✓ Used to study chemical equilibrium and kinetics

✓ Fluorescence tags/markers

✓ Important for various organic-inorganic complexes

✓ Sensitivity to local electrical environment polarity, hydrophobicity

✓ Track (bio-)chemical reactions

✓ Measure local friction (micro-viscosity)

✓ Track solvation dynamics

✓ Measure distances using molecular rulers: fluorescence resonance energy transfer (FRET)

✓ Band gap of semiconductors

✓ Nanomaterials characterization

Conclusions

✓ Luminescence spectroscopy provides complex information about the defect structure of solids
  - importance of spatially resolved spectroscopy
  - information on electronic structures

✓ There is a close relationship between specific conditions of mineral formation or alteration, the defect structure and the luminescence properties (“typomorphism”)

✓ Useful for determining semiconductor band gap, exciton energy etc.

✓ For the interpretation of luminescence spectra it is necessary to consider several analytical and crystallographic factors, which influence the luminescence signal

Questions ?

Thanks