

# SPECIAL CHARACTERISATION OF HETEROCYCLIC COMPOUNDS

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*Abstract:* - The present work embodies the observations of spectroscopic studies fluorescence spectroscopic, fluorescing abilities by recording fluorescence in liquid and solid matrices. A CNDO/S-CI calculation is used to know the electronic energy levels in laser dyes coumarin and its various substituted derivatives. Effect of solvents and substituents on the fluorescence spectra of dyes coumarin derivatives has also been studied. Upon excitation dipole moment of coumarin dyes changes which is estimated using solvato-chromic theories and tried to explain in terms of resonance structures. The percentage polarization of fluorescence emission has also been measured in different organic solvents. Molecule on absorption of light get excited and subsequently emit photons is known as fluorescence. It take place due to the transition between excited and ground states of the same multiplicity in a time period of  $10^{-11}$  to  $10^{-7}$  second after excitation. However, when emission occur from transition between states of different multiplicity, usually from a triplet excited state returning to a singlet ground state, is termed a phosphorescence. Besides these, there are other types of luminescence as well; for example, electroluminescence and chemiluminescence. The former take place when electrical energy excites molecules or atoms, whereas the latter is caused by a chemical reaction. Bioluminescence is a special example of chemiluminescence in which light is emitted by living organisms due to cellular oxidation of some substrate in the presence of an enzyme.

Key words: coumarin, CNDO/S-CI fluorescence emission, electroluminescence, fluorescing abilities, chemiluminescence, Bioluminescence.

## INTRODUCTION

Organic compound shows the phenomenon of fluorescence due to the delocalisation of electron, obtained from conjugated system. Fluorescence of molecule in solution causes due to the transition from the lowest vibrational level of the first excited singlet to the ground state. In aromatic molecules electrons are delocalised hence the coupling strength between the excited singlet electronic states is much stronger than that exist between an excited electronic state and the ground electronic state. The higher excited singlet states lie very close to each other in comparison with the separation between the first excited singlet electronic state and the ground state resulting in the mixing of their vibrational levels. According to Franck Condon principle a molecule by the absorption of radiation jumped from ground state to the vibration level of any such higher electronic state, and also on reduction of kinetic energy, it can jump to higher vibrational level of an adjacent lower electronic state. This process of energy transfer is known as internal conversion. The internal conversion and the vibrational deactivation through thermal relaxation, leave the molecule in the lowest vibrational level of the first excited singlet electronic state before it starts radiation through quantum jump to the ground state. Therefore, the resulting fluorescence quantum is of lower energy than the absorbed one, which shifts the fluorescence spectrum towards the longer wavelength side as compared with absorption spectrum.

The most extensive investigation being one by Heller. The application of lanthanide ions in luminescent materials for displays device, laser applications. Weber [1971] and upconverter phosphors. Johanson [1972] has lead to intensive study of the emission characteristics of these ions in various crystalline environments. Almost all such investigations have been undertaken for lanthanides in non centrosymmetric environments. Reisfeld [1976]. So that the f-f electric dipole no phonon transitions become allowed. Excited state of lanthanide ions in centro-symmetric environments should have much longer relaxation times.

## RESEARCH METHODOLOGY

The absorption of electromagnetic radiation is a universal property of matter. Atoms and molecules may occupy one of the several stable electronic states  $E_n$ . Light can only be absorbed if the energy ( $h\nu$ ) of a photon corresponds exactly to the difference between two such states, which is of the order of an electron Volt (eV). Each electronic state in turn is composed of a large number of vibrational states, separated by the energies of the order of .1 eV. The vibrational states gets further split into rotational states, spaced approximately .01 eV apart. Rotational states are frequently observed in the ultraviolet (u.v.) and visible regions only for gases. Both the absorbed light intensity transmittance (optical density), and the positions of the bands (energy), contribute much to the characterization of an absorption spectrum. Useful information can only be obtained from the uv or visible spectrum of a compound if the wavelength of the absorption bands and their intensities must be measured accurately. The compound should be soluble in some suitable solvent (matrix) that does not itself absorb light in the region under investigation. Generally common solvents such as 95% ethanol, water, hexane and cyclohexane are used. The positions of the absorption peaks of a organic compound depends upon dielectric constant of solvent, (matrix shift) resulting in the shifting of the peaks i.e. Thus the spectra of coumarin laser dyes have been recorded in various polar and nonpolar matrices.

We have recorded the uv-visible absorption and fluorescence emission spectra of substituted coumarins in different organic solvents of different polarity. We have interpreted the spectra of coumarin dyes by calculating their transition energies and comparing them with the experimental results.

The subsequent electronic stage compares the signal from the sample cell and the reference cell, so that the chart recorder or digital recording system can record the difference or the ratio of the two. To achieve this, modulation of the two light beams with different phase is required. The wavelength of the light is scanned by a motor which drives the monochromator setting, and the recorder is advanced synchronously. An unambiguous assignment of recorder position to wavelength may be achieved in this way. The presentation of the measured signal is either linear, showing transmittance in percent, or logarithmic, giving optical density or extinction.

## OPTICAL SYSTEM

The model V-570 measures the absorption spectrum in the wavelength region 190-2500 nm. The schematic diagram of the optical system of this absorption spectrophotometer is shown. A deuterium discharge tube (190 to 350) is used for the ultraviolet and a tungsten iodine lamp (350 to 2500) is used for the visible and near infrared region, as the light sources. The light from the light source is converged and enters the monochromator. It is dispersed by the grating into the monochromator and the light coming out through the exit slit is monochromatic. This monochromatic light is split into light paths by a sector mirror, one incident on the sample to be measured and the other on the reference sample such as solvent or other. Two rectangular quartz cells with cover are used to record the spectra of Coumarin dyes in organic solvents. The light that has passed through the sample or reference sample is incident on the photomultiplier tube or PbS photoconductive cell depending on the wavelength range.

## ELECTRICAL SYSTEM

The electrical system configuration. The light fall on the photomultiplier tube or PbS photoconductive cell get converted into an electrical signal and after being synchronously rectified is converted into a digital form and enters the microcomputer. The signal processed by the microcomputer is displayed on the output device as digital data or spectrum.

Light source changeover, wavelength drive, slit drive, filter drive etc are all controlled by the microcomputer.

## BASIC PRINCIPLE AND TECHNIQUE USED IN FLUORESCENCE SPECTROFLUORIMETER:

A major difference between fluorescence and absorption instrument lies in the geometry of the sampling area. For absorbance measurements the beam travels straight across the sample position and only the reduction in its intensity after it has passed through the sample is considered. In fluorescence measurements we have to observe the fluorescence emission in the presence of much stronger exciting radiation. Although this is possible with the 180° 'straight' through geometry because the incident and emitted radiation is of different wavelength, the unabsorbed incident radiation passes into the monochromator and gives rise to serious stray light problems. A much more satisfactory arrangement is to view the fluorescence at 90° to the incident

beam. This is possible because fluorescence is emitted in all directions from the sample. Direct light cannot then enter the monochromator though some radiation at the incident wavelength always accompanies the fluorescence radiation as a result of scattering from solvent molecules which is often of comparable intensity with the fluorescence of the solute. If the fluorescent species is at very low concentration, Rayleigh scattering becomes troublesome and a further problem arises from the Raman scattering of the solvent. Although this is very much weaker than Rayleigh scattering, it occurs at longer wavelengths and in many cases overlaps and interferes with the emission bands of the fluorescent species. If the sample contains suspended particles this makes further contribution to the scattering at the exciting wavelength through Tyndall scattering. This can be far more intense than Rayleigh scattering if the sample is all turbid and can give rise to high stray light levels. The 90° configuration is of great importance in spectrofluorimetry and makes a very significant contribution to the high sensitivity of the technique. This can reduce the problem from turbid and solid solutions. In this geometrical configuration a more powerful source has to be used. Two wavelength selectors are required to control the wavelength of the incident and emitted radiation independently.

### SOL-GEL MATRIX PREPARATION

The selection of proper matrices for doping of organic molecules is one of the important aspects in sol-gel materials that needs due consideration. An essential property of the host matrix is to have an optical window- a region of zero absorption extending over the absorption and emission bands of the molecule. While the positions of the absorption and emission bands of the fluorescent molecules are very similar in the hosts, the intensities of the bands depend strongly on the molecule host interaction and cannot be considered as an intrinsic property of the ion itself. One of the key problems in the applications of solid state laser materials, Nusses [2012], is the investigation and application of host matrix. Attempts have been made to fabricate solid state materials, Acheson [1977], using organic solid hosts. These organic host materials, however, seem to be inferior to inorganic host materials lacking effective mechanical, thermal and chemical properties, photostability and various optical properties. In general, the inorganic materials, Behmenburg [1978], are found to have superior optical, thermal and chemical properties. It has been found that solgel matrix is not reactive with the doped organic molecules serves as a good solvent for solutes to be studied. A good solubility of the matrix is also helpful to obtain good concentration of molecules. does not absorb in the spectral region of interest is not much affected by humidity and atmospheric gases can be easily prepared at room temperature.

### Results and Discussion:

Absorption spectra of 4-hydroxy-6chloro coumarin in different solvents. Where as the effect of solvent on absorption spectrum of 4-hydroxy-6-chloro coumarin is given in Fig. 7.26 and the effect of concentration of 4-hydroxy-6-chloro coumarin in different solvent. The absorption spectrum of 4-hydroxy-6-chloro coumarin in sol-gel matrix at different concentrations.

Fusion of a benzene ring to the heterocyclic nucleus causes a bathochromic shift and raises the intensity of absorption with a corresponding decrease in the life time in the excited state before spontaneous emission occurs. Thus quonoline, isoquinoline and indole and quinolinium and isoquinolinium ions fluorescence in the ultra violet compounds derived from oxygen containing heterocyclic rings fused to  $\alpha$ -benzene ring often fluoresce visibly. Coumarin itself benzo- $\alpha$ -pyrone fluoresces only in the ultraviolet but some of the hydroxy and amino derivatives fluoresce visibly. Umbelliferone 7-hydroxy coumarin, fluoresces blue, while aesculin, long known as the fluorescent material in the extract of horse chest nut bark is the glucoside of 6,7-dihydroxy coumarin, 7-amino coumarin is also fluorescent.

Derivatives of benzo-v-pyrone are also visibly fluorescent, especially as the oxonium salt in concentrated sulphuric acid. Flavone for example fluoresces violet in concentrated sulphuric acid. Morin is a pentahydroxy flavone used in the detection of aluminium which forms a green-fluorescing complex Jayanthi [2017]. Sulphur containing heterocyclic compounds may also fluoresce. Xanthione the sulphur analogous of xanthone is visibly coloured and fluoresces red; dibenzothiophene sulfonic acids fluoresce violet, as does sulfonated 2-p-amino phenyl-6-methyl benzothiazole.

We have noticed eleven electronic transitions on the basis of CNDO/S-CI calculations in 4-hydroxy-6-chloro coumarins. Out of eleven transitions two are very weak. along with principal band and calculated visual intensities. CNDO/S-CI calculations predict three very strong bands of comparable intensity at 722.1 nm (1.94 eV). The strongest band (Si) of maximum intensity occurs

at 201.3 (nm). The second strong calculated band is found at 196.9 nm, where as the third maximum intensity band fall at 313.7 nm.

It is ascribed as belonging to transition  $x$ - and present at 313.7 nm (3.82 eV). In addition to these three bands, of maximum intensity, along the side two bands of medium intensity are noticed at 225.8 nm (0.1636) and 278.7 nm (4.32). Apart from the above five bands, three bands of comparatively less intensity also have been noticed as 250.7 nm, 279.1 nm, and 215.8 nm. Besides this one more electronic transition band of medium intensity has been appeared at 211.3 nm.

### CONCLUSION:

In the present Investigation we have used hetrocyclic compounds. We have used organic laser dyes coumarins and its derivates and we have studied the behaviour of solvents on absorption spectra. In this study we have noticed that the how dipole moment of dyes coumarins changes and electronic energy laves in laser dyes. Molecular structure and properties are also discussed in the present work. Percentage of polarization of fluorescence emission of coumarin (methyl, phenyl, methoxy and amino group) in different organic solvents have been studied. Experimental results are in comfirmations with the theoritical Results based on perrins theory. Sol-gel matrix has been used to study the change of matrix and concentration on spectra. In industries this technique is used frequently. In manufacturing of dyes the study is very useful. In future by changing the percentage of compounds used will give better results.

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