SYNOPSIS OF THE THESIS ENTITLED

STUDY OF PHOTOPHYSICAL PROPERTIES OF SOME ORGANIC COMPOUNDS

Photoexcitation and subsequent events which lead from one to another state of molecular entity through radiation and radiationless transition without change in chemical change is termed as Photophysical process. Photo physics of organic molecules has been field of interest because understanding of the excited state properties helps in exploring various phenomenons taking place in these systems. This study may help not only to design of new molecules but also to explore the possibility of various applications. Some of these applications include, laser dyes, probes for – polymers and biological systems, chemical sensors and molecular switches et.,[1,2].

Various theoretical and experimental methodologies are available to study the photo physical properties of organic molecules. Under experimental methods, luminescent measurement technique has been widely used. Luminescence can be broadly defined as the phenomenon in which emission of electromagnetic radiation takes place by system after its excitation. Luminescence exhibited by organic molecules is classified into Fluorescence, Phosphorescence and delayed fluorescence. In the fluorescence, the molecule after the process of excitation the fluorescence emission takes place within $10^{-8}$ second. The fluorescence radiation is due to allowed singlet-singlet transition and decays exponentially. If the radiation decays exponentially with longer decay times and at longer wavelengths compared to that of fluorescence, it is called phosphorescence and is due to triplet-singlet transition, which is forbidden. If the radiation decays non-exponentially over longer times with same spectrum as in fluorescence, it is called delayed fluorescence and is due to the thermal excitation of the triplet state to the first excited singlet state leading to the allowed singlet-singlet transition.[3,14] Here, fluorescence technique is employed to study one of the photophysical properties that is electronic excitation energy.
transfer in molecular entity. A molecular entity consists a minimum of binary molecular system. The phenomenon of excitation energy transfer from the excited molecules to the unexcited molecules involves various photo physical processes. Here, fluorescence quenching study is employed since this is one of the energy transfer mechanism in molecular entity. The other important photophysical property study carried out here is the estimation of ground state and excited state dipole moments of the organic molecules. This study is also of interest because knowledge of dipole moments is useful in extracting parameters like polarizability in non-linear optical materials, understanding nature of the emitting state and determining the tunability of the emission energy as a function of the medium. There are various techniques available for estimation of ground state and excited state dipole moments of organic molecules. Here, solvatochromic method is employed for estimation of excited state dipole moment.[4,5].

The study of energy transfer processes in organic liquid system is has been subject of intensive investigation. The study of energy transfer processes becomes much simpler if the solute molecules are excited directly and an appropriate external quencher added quenches the excited solute molecules. Energy transfer mechanism in molecular entity is sensitive to environments such as viscosities, dielectric constants, temperature and so many other factors. An intensive investigation of the environmental dependence of these has been the subject of the part of our work. The experimental techniques employed for understanding the nature of fluorescence quenching phenomenon in molecular entity are steady state and transient state methods. Following theoretical models are used for fluorescence quenching studies, to analyze the data

1) Stern–Volmer equation
   i) Collisonal quenching (Short range quenching)
ii) Static and dynamic quenching
   a) Ground state complex formation
   b) Sphere of action static quenching

2) Dynamic quenching
   i) Time dependent quenching
   ii) Finite sink approximation

In earlier days fluorescence quenching studies were quite widely used in scintillation detector [6]. In recent times, fluorescence quenching is widely used as probe in many bioanalytical applications. These include the extent of exposure of the probed groups, the microenvironment in which these groups exist and overall conformation of the macromolecules and its dynamics. This phenomenon is also used in many chemical optical sensors to many chemical species [7-10]. Keeping all these facts in view we thought study of fluorescence quenching might explore some new avenues and at the same time it may help to enrich the knowledge further.

Nature of charge distribution in the molecule can be understood in simpler way with the knowledge of dipole moments in the ground and excited states. Nature of charge distribution in the molecule can be studied using absorption and fluorescence characteristics in different solvents. The effect of solvent on the absorption and fluorescence characteristics of organic compounds has been a subject of interesting investigation [11,12]. Excitation of a molecule by Photon causes a redistribution of charges leading to conformational changes in the excited state. This can result in an increase or decrease of dipole moment of the excited state as compared to ground state. Here, Solvatochromic method is employed to estimate excited state dipole moment of the molecules. Solvatochromic method is based on the shift of absorption and fluorescence maxima in different solvents of varying polarity. Koutek has shown that under suitable
conditions, the solvatochromic method yields fairly satisfactory results [13]. However, for the estimation of excited state dipole moment knowledge of ground state dipole moment is necessary hence, one of the theoretical methods suggested by Guggenheim is used for estimating ground state dipole moment of the molecule. In order to estimate excited state dipole moment three methods namely Lippert’s, Bakshiev’s and Chamma-Viallet’s are employed.

For the study of fluorescence quenching and estimation of ground and excited state dipole moments three molecule/solutes are used. These are the synthesized molecules procured from the Department of Chemistry, Karantak University Dharwad. Three molecule are 4-(2,6-Dibromo-4-methyl-phenoxy methyl)-benzo [h] chromen- 2-one, 4-(6,7-Dimethoxy-3,4-dihydroisoquinoline-1-ylmethyl)-6-methyl- chromen-2-one and 6-Methoxy-4-p-tolyoxymethylchromen-2-one respectively.

Thesis comprises of eight chapters, first chapter gives a brief introduction on the phenomenon of energy transfer/fluorescence quenching in molecular entity and estimation of dipole moments both in ground and excited states.

Second chapter discusses the theories relating phenomenon of quenching of excitation energy of solute molecules and estimation of ground and excited state dipole moments. Survey of literatures relating to these studies has been included at the end of this chapter. Third chapter discusses briefly the materials and the experimental methods used in these studies.

Chapter four gives experimental procedure and the results obtained under steady state and transient state methods for three solutes in different solvents with aniline as quencher. The three solutes used here are i) 4-(2,6-Dibromo-4-methyl-phenoxy methyl)-benzo [h] chromen-2-one ii) 6-Methoxy-4-p-tolyoxymethyl-chromen-2-one iii) 4-(6,7-Dimethoxy-3,4-dihydro-
isoquinoline-1-ylmethyl)-6- methyl chromen 2-one and the solvents used are toluene, benzene, acetonitrile, dimethyl formamide, tetra-hydrofurane, dioxane tetra-chloro ethylene, trichloro ethylene, dimethyl sulfoxide and acetone. Transient method is also performed for all the three solutes in toluene solvent only. Experimental data follow linear Stern-Volmer equation hence; data were analyzed using linear Stern-Volmer equations both in steady state and transient state methods. Based on the magnitudes of rate parameters, phenomenon of fluorescence quenching is mainly attributed to collisional (Short range) quenching.

Chapter five discusses the experimental procedure and results obtained for steady state fluorescence quenching of 4-(2,6-Dibromo-4-methyl-phenoxymethyl)-benzo [h] chromen-2-one in Trichloroethylene, acetone and Tetrachloroethylene solvents, 6-Methoxy-4-p-toloyxymethyl-chromen-2-one in Trichloroethylene and Tetrachloroethylene solvents and 4-(6,7-Dimethoxy-3,4-dihydro-isoquinoline-1-ylmethyl)-6-methyl-chromen-2-one in acetone and Dimethylsulphoxide. Experimental data follow non linear (i.e positive deviation) Stern-Volmer equation hence, data were analyzed using the theories relating non-linear Stern-Volmer equation. Based on the magnitudes of the rate parameters estimated, phenomenon of quenching in these systems is attributed to static and dynamic quenching.

Chapter six discusses the experimental procedure and results obtained by steady state measurements for the two solutes namely, 4-(2,6-Dibromo-4-methyl-phenoxymethyl)-benzo [h] chromen-2-one and 6-Methoxy-4-p-toloyxymethyl-chromen-2-one in media of varying dielectric constants comprising of benzene (BN) and acetonitrile (AN) added in different proportions by volume. In both cases aniline were used as quencher. Other solute namely, 4-(6,7-Dimethoxy-3,4-dihydro-isoquinoline-1-ylmethyl)-6-methyl-chromen-2-one was not studied since it does not show positive deviation that is the effect of solvent polarity on this solute is not
observed. Experimental data follow nonlinear Stern-Volmer equation hence; data were analyzed using the theories relating to nonlinear Stern-Volmer equation. Based on the magnitudes of the rate parameters estimated, phenomenon of quenching in these systems is attributed static and dynamic quenching.

Chapter seven discusses the experimental procedure and the results obtained in the estimation of ground state and excited state dipole moments for three organic molecules namely, 4-(2,6-Dibromo-4-methyl-phenoxymethyl)-benzo [h] chromen- 2-one, 4-(6,7-Dimethoxy-3,4-dihydro-isoquinoline-1-ylmethyl)-6-methyl- chromen-2-one and 6-Methoxy-4-p-tolyoxymethyl-chromen-2-one.

Chapter eight gives the brief summary of the experimental results and conclusions drawn in each chapters of four, five, six and seven respectively.

The thesis contains list of references at the end of each chapters.
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