Sudan University of Science and Technology

College of Graduate Studies

Study of Stoke and Amplified Spontaneous Emission Properties of some Diamino Phenyl Propen Derivatives

دراسة ستوك وخصائص الإنبعاث التلقائي المتخضم من بعض مشتقات داي اماينو فينايل بروبين

A Thesis Submitted for Fulfillment of PhD Degree in Physics

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قال تعالى: ﴿إِنَّ اللَّهَ وَمَلَائِكَتَهُ يُصَلُّونَ عَلَى النَّبِيِّ يَا أَيُّهَا الَّذِينَ آمَنُوا صَلُّوا عَلَيْهِ وَسَلِّمُوا تَسْلِيمًا﴾

[الأحزاب: 56].

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ملخص البحث

في هذا البحث تم تصنيع ثلاث اصباغ عضوية تسمى الشالكونات، تمت ودراسة الخصائص الطيفية و اليزرية لهذه الصبغات تحت تراكيز ومحاليل عضوية مختلفة. اثبتت التجارب أن هذه الشالكونات لها ازاحة ستوك (Stokes' Shift) و ناتج كمي للانبعاث (Quantum Yield) عالٍ مقارنة مع الصبغات الليزرية التقليدية الأخرى مثل سلاسل الكومارين والرودامين. عند تراكيز ومذيبات مناسبة وطاقة ضخ بواسطة مصدر ليزر :Nd YAG- (355 نانومتر)، اظهرت هذه المواد أطيافا ليزرية ذات أطوال موجية مختلفة معتمدة على التركيب الكيميائي لها والمحلول الذي اذيبت فيه حيث كان المدى الطيفي بين 535nm و 570. ومن جانب آخر أثبتت الدراسات أن هذه الصبغات تتميز باستقرارية ضوئية وكسب ليزري عالٍ مقارنة بالصبغات التقليدية الأخرى .

Study of Stoke and Amplified Spontaneous Emission Properties of 3-(4-(dimethylamino) phenyl)-1-phenyl-(2E)-propen-1-one, 1-(4-chloridephenyl)-3-(4- N, N dimethyl amino phenyl)-2-propen-1-one and 1-(4-methylphenyl)-3-(4- N, N-dimethyl amino phenyl)-2-propen-1-one

Abstract

This study comprises the synthesis and spectral properties of three chalcones 3-(4-(dimethylamino)phenyl)-1-phenyl-(2E)-propen-1-one (DMAPPP),1-(4-methylphenyl)-3-(4- N, N-dimethyl amino phenyl)-2-propen-1-one (MDMAPP) and 1-(4-chloridephenyl)-3-(4- N, N dimethyl amino phenyl)-2-propen-1-one (CPDAPP) in several organic solvents have been studied. Photophysical characteristics such as absorption, fluorescence spectra, stokes' shift, fluorescence and quantum yield of these chalcones were measured in different solvents and concentrations. The amplified spontaneous emission (ASE) performance of these dyes under various concentrations, organic solvents and pump pulse energies of Nd: YAG lasers (355nm) were investigated. The gain and the effect of concentration and pump power energies of these chalcones were obtained. The most important features are chalcone has an excellent photochemical stability the ASE emission from the chalcone is tunable in the wavelength region between 535 and 570nm.

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CHAPTER I

1. Introduction

1.1. Laser Dyes

The materials, which give color to your clothes and add luster to the face creams are organic compounds, called dyes. When these are dissolved in organic liquids (like, ethanol, chloroform, etc.) the solution becomes highly fluorescent (Recall the fluorescent paints used for warning signals). These dye solution have proved to be excellent media for laser action [1, 2].

Laser dyes are large organic molecules with molecular weights of a few hundred. When these organic molecules are dissolved in a suitable solvent such as benzene, methanol, or acetone, can be used as lasing media in a dye laser. Laser dye solutions absorb at shorter wavelengths and emit at longer wavelengths. Many different dyes are nowadays available, and in total they can cover huge wavelength regions like exalite, coumarin, rhodamine, pyrromethene, pyridine, fluorescein, pyridine or crystal can characterize a whole family of dyes with slightly different chemical structures, having somewhat different ranges of emission wavelengths and being distinguished with additional numbers. For example, one may use coumarin 2, 47, 102 or 153 for lasers in the blue to green spectral region [3].

Note that many laser dyes and some of the used solvents are poisonous and partly also carcinogenic. One should therefore carefully avoid to expose the skin to such a dye solution, or even to spill the dye by operating a not properly assembled dye circulating system. A particularly hazardous solvent, sometimes used for cyanide dyes, is dimethy lsulfoxide (DMSO), which greatly accelerates the diffusion of dyes into the skin [3].

When we dissolve laser dyes in a different type of organic solvent, they will produce a different absorption and fluorescence spectra peaks; this is what distinguishes liquid as an active lasing medium compared by gas and solid-state lasing
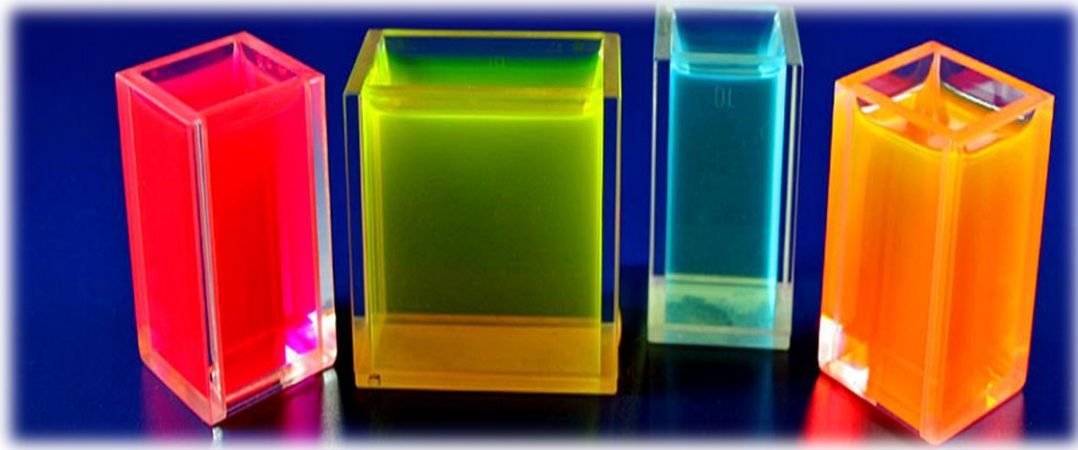
Fig.1.1 Laser Dyes in some organic solvents

1.2. Dye Lasers

A dye laser is a laser which uses an organic dye as the lasing medium, usually as a liquid solution. Compared to gases and most solid state lasing media, a dye can usually be used for a much wider range of wavelengths. The wide bandwidth makes them particularly suitable for tunable lasers and pulsed lasers. Moreover, the dye can be replaced by another type in order to generate different wavelengths with the same laser, although this usually requires replacing other optical components in the laser as well [4].

The development of the dye laser has been intimately tied to the systematic search for organic dye structure and dye media in which stimulated emission is observed. An array of photophysical properties such as absorptive, emission (fluorescence) yield, stokes shift, and triplet formation influence the threshold and peak power lasing characteristics. The tailoring of dyes must also be contend with variables

having to do with photochemical reactions which degrade dye and produce competitively absorbing product, thus influencing dye service life as other parameters. In the first comprehensive review of laser-dye structures and properties, Drexhage, compiled a table of about three hundred dyes that had been found to laser reasonably. In a later survey covey covering reports on laser dyes through 1980, it has been identified that 546 dyes from various classes of structure work well [5-7].

With the advent of powerful laser or flash lamp pump sources and needs for high output and repetition rate, the requirements for photochemical stability of lasing media are extreme. For pulsed lasers, projections as high as 100W power, pulse frequency at 500Hz and 200mJ/pulse have been made. In a review of advances in laser-dye development notes that, the barrier to wider industrial use of the dye laser is due association with dye instability (photo degradation). The service life of a typical rhodamine dye in alcohol on excitation with the unfiltered light of a bank of flash lamps is limited to a few flashes [8].

1.3. Laser

A **laser** is a device that emits light through a process of optical amplification based on the stimulated emission of electromagnetic radiation. The term "laser" originated as an acronym for "**light amplification by stimulated emission of radiation**". A laser differs from other sources of light because it emits light coherently. Spatial coherence allows a laser to be focused to a tight spot, enabling applications like laser cutting and lithography. Spatial coherence also allows a laser beam to stay narrow over long distances (collimation), enabling applications such as laser pointers. Lasers can also have high temporal coherence which allows them to have a very narrow spectrum, i.e., they only emit a single color of light. Temporal coherence can be used to produce pulses of light—as short as a femtosecond [9-12].
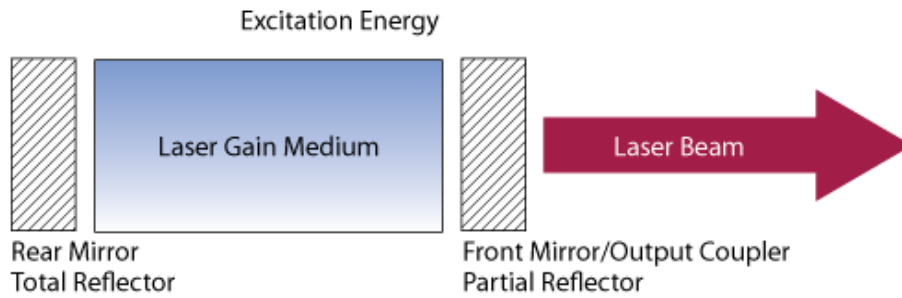
Fig.1.2 Laser components

1.3.1. Active laser media

The active laser media (gain media or lasing media) is the source of optical gain within a laser. The gain results from the stimulated emission of electronic or molecular transitions to a lower energy state from a higher energy state previously populated by a pump source [13, 14].

Examples of active laser media include:

- Certain crystals.

- Glasses.

- Gases.

- Semiconductors.

1.3.2.How dose Laser Works

The lasing medium will normally emit photons in specific spectral lines when excited by an energy source. The wavelength is determined by the different quantum levels, or energy states, of the material. Normally, most atoms in a medium are in the ground state. Some small percentage will exist at higher energies as well. Normally, these higher energy states are unstable and the electrons will release this excess energy as photons almost immediately and return to the ground state. In some materials,

specifically those chosen as lasing medium, a metastable state is possible where the atom or molecule will remain at an excited state for some time [15, 16].

Energy is supplied to the laser medium by the energy pumping system. This energy is stored in the form of electrons trapped in the metastable energy levels. Pumping must produce a population inversion (i.e., more atoms in the metastable state than the ground state) before laser action can take place [17].

When population inversion is achieved, the spontaneous decay of a few electrons from the metastable energy level to a lower energy level starts a chain reaction. The photons emitted spontaneously will hit (without being absorbed)other atoms and stimulate their electrons to make the transition from the metastable energy level to lower energy levels - emitting photons of precisely the same wavelength, phase, and direction [18].

This action occurs in the optical cavity. When the photons that decays in the direction of the mirrors, (most are lost - lasers are not as efficient as one would believe) reach the end of the laser material, they are reflected back into the material where the chain reaction continues and the number of photons increase. When the photons arrive at the partially-reflecting mirror, only a portion will be reflected back into the cavity and the rest will emerge as a laser beam [16] . (**Fig 1.3**) shows the steps of producing the laser beam.
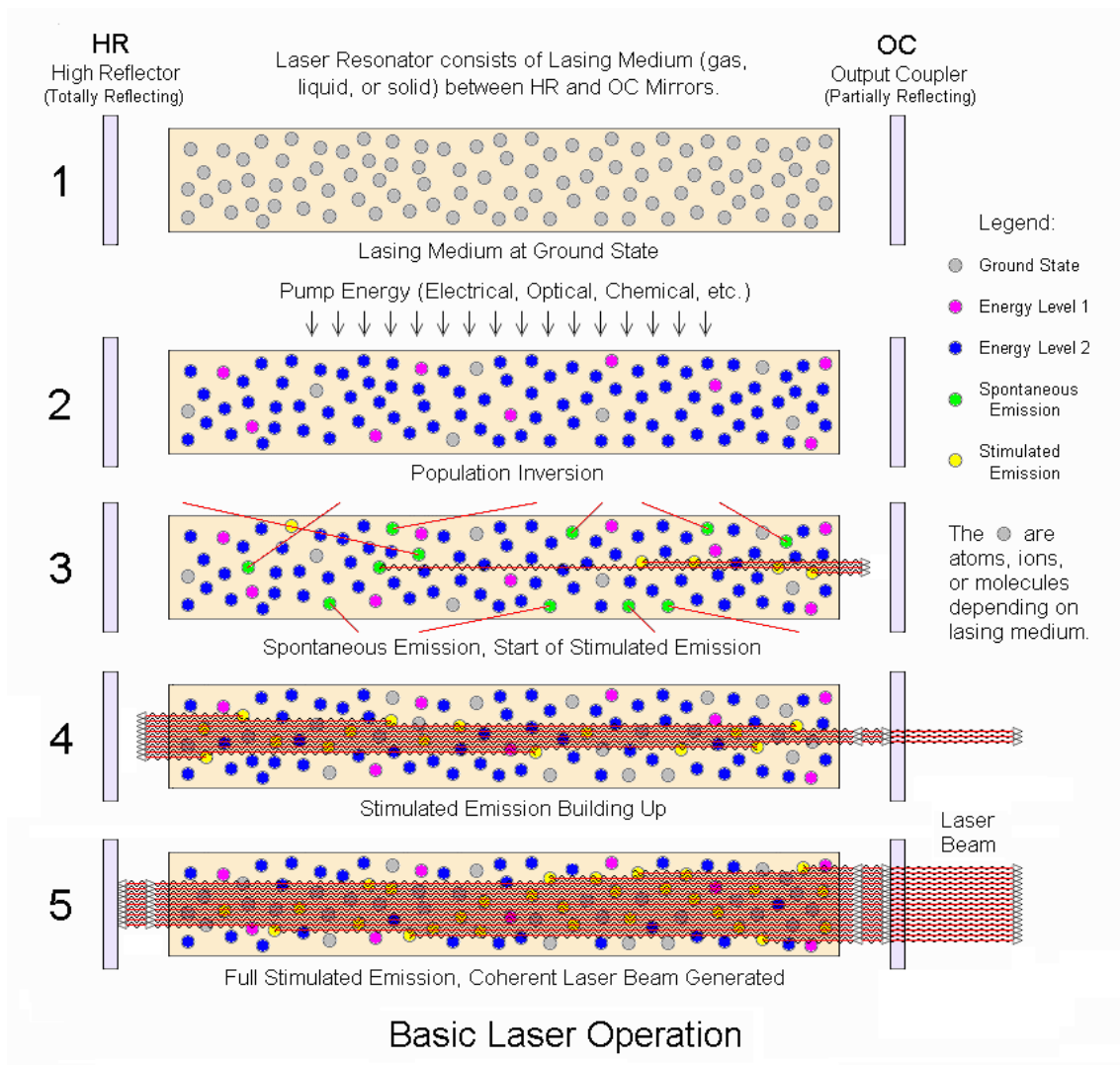
Fig.1.3 Basic Laser Operation

1.3.3. Types of lasers

There are many types of lasers available for research, medical, industrial, and commercial uses [19].

1- Gas laser: for example He Ne laser, CO_2 laser

2- Solid state laser: Titanium-doped sapphire, Nd: YAG.

3- Semiconductor laser: Diode Laser

4- Liquid laser(dye laser): coumarin, rhodamine

5- Free electron laser:

1.4. Chalcone

Chalcones are natural as well as synthetic yellow crystalline compounds having general molecular formula of C6H5CH=CHCOC6H5. It is could be obtain using simple condensation reaction of Benz aldehyde and acetophenone in ethanol as solvent and basic condition [20-22] as shown in the (**Fig 1.4**) below. Also the chalcone can be synthesized form the derivatives of this compound, several of which are plant pigments related to the flavones
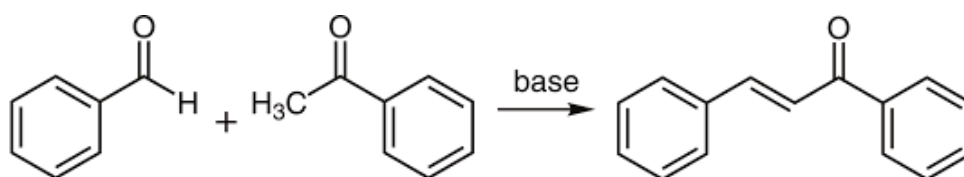
Fig.1.4 Rote synthesis of chalcone

Chalcones are organic compounds with a unique structural feature of having a carbonyl functional group in conjugation with carbon-carbon double bond and the whole molecule is in conjugation. The presence of α, β- unsaturated keto group or enone function, is found to be responsible for their biological activity [23, 24].
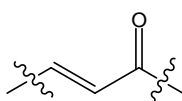
Fig.1.5 Enone functional group

1.4.1. Properties of Chalcone

The conjugation of π electrons in the enone function gives the chalcone some of the extra stabilization which is normally the conjugation with the two benzene rings in their structures. The expected characterization of this enone function by the methods

of spectroscopy is one of the most important guides to make sure that the chalcone has been formed[25]. Different spectral properties have been reviewed [26, 27].

1.5. Problem statement

Production of low cost laser is one of the most important issues that attracts high attention in last few years. New laser media from organic compounds, called chalcone dyes will offer cost effective media to produce very promising dye laser which can be candidate as the cheapest and most suitable dye media. The recognized wavelength agility these lasers can offer very large pulsed energies or high average powers.

In spite of consider number of dyes is used in food manufacturing and coloring, most dyes are carcinogenic and very toxic. This work introduced new dyes which are not toxic and environmentally friend to produce dye lasers .

The application of dye lasers in manufacturing and medicine fields is still limited due to carcinogenic and very toxic characteristics of the most dye lasers. In addition most of them are very corrosive to all metals except stainless steel. The new chalcone dyes that synthized in this research (1-(phenyl)-3-(4- N, N dimethyl amino phenyl)-2-propen-1-one (DMAPPP), 1-(4-chloridephenyl)-3-(4- N, N dimethyl amino phenyl)-2-propen-1-one (CPDAPP) and 1-(4-methylphenyl)-3-(4- N, N dimethyl amino phenyl)-2-propen-1-one (MDMAPP)) will open new widows to use dye laser without carcinogenic and toxic and corrosion effects to be combatable for wide range of applications .

A wide variety of solvents can be used, although most dyes will dissolve better in some solvents than in others. Some of the solvents used are water, glycol, ethanol, methanol, hexane, cyclohexane, cyclodextrin, and many others. Solvents are often highly toxic, and can sometimes be absorbed directly through the skin, or through inhaled vapors. Many solvents are also extremely flammable. The various solvents can also have an

effect on the specific color of the dye solution, the lifetime of the singlet state, either enhancing or quenching the triplet state, and, thus, on the lasing bandwidth and power obtainable with a particular laser-pumping source. This work covers Nemours of solvents to and optimized the best conditions and solvent.

1.6. Motivations

The dynamics of the spectral properties of these chalcones and related heterocyclic compounds have not been fully established yet for laser application. In this work, these spectral properties are fully described by the excited state dynamics of chalcones in nano, pico and femto second time domain for all transient states.

1.7. Objectives

The aim of this research is to introduce new laser media from organic compounds, called chalcone dyes. To design systematically to study the effect of the donor and acceptor auxochromes as well as their position to study: (a) The spectral properties of three chalcones (b) The spectral tuning of the ASE (without feedback) for three chalcone dyes(c) the Optical gain. These steps will be repeated for different temperature & Solvent environment. Furthermore, the details of this aim can be summarized as:

1. To synthesis and characterize the 1-(phenyl)-3-(4- N, N dimethyl amino phenyl)-2-propen-1-one (DMAPPP) via condensation reaction between acetophenone and 4-dimethylaminobenzaldehyde in basic condition of sodium, in ethanol for laser media application.

2. To synthesis and characterize Synthesis of the 1-(4-chloridephenyl)-3-(4- N, N dimethyl amino phenyl)-2-propen-1-one (CPDAPP) by using a condensation reaction of 4-dimethyl amino benzaldahyde and 4-chloroacetophenpne in basic

condition of Sodium Hydroxide in ethanol, and to exam the laser activity of this material under different conditions.

3. To synthesis and characterize the 1-(4-methylphenyl)-3-(4- N, N dimethyl amino phenyl)-2-propen-1-one (MDMAPP) prepared by a green synthesizing method of condensation reaction between 4-dimethyl aminobenzaldahyde and 4-methylacetophenpnein basic condition of Sodium Hydroxide dissolved in ethanol, and to investigate the laser activity of the obtained product under different conditions to be used as laser media.

1.9. Thesis outlines

Chapter II deals with literature review of chalcones. Chapter III we had constructed the theoretical background of the laser dyes such as: absorption, fluorescence, quantum yield of fluorescence, fluorescence lifetime, Stokes Shift, dye Photophysics, theory of amplified spontaneous emission, laser structures, dye laser pumping techniques, solvent effects on dye emission parameters and the concentrations effect. Chapter IV, deals with experimental techniques such as: solvents and chalcones, UV-VIS absorption and fluorescence, Nd: YAG laser, charge-coupled device and ASE setup. Chapter V, deals with the results and discussion of the study of on the spectral properties of three chalcones, under different organic solvents and concentrations. The Amplified Spontaneous Emission characteristics of three chalcones under pulsed laser excitation characteristics in few organic solutions were studied and compared with some other conventional laser dyes. Chapter VI dealing with the conclusions and recommendation as last chapter.

CHAPTER II

2. Literature Survey

2.1. Importance of Laser

The importance of laser tenability is due to wide application at many disciplines [28] , and there are many pervious works reported the importance of the laser in its appellations in different fields such as:

2.1.1. Industrial Applications of Laser

Today, laser can be found in a broad range of applications within industry, where it can be used for such things as pointing and measuring [29] . In the manufacturing industry, laser is used to measure the ball cylindricity in bearings by observing the dispersion of a laser beam when reflected on the ball [30].Yet another example is to measure the shadow of a steel band with the help of a laser light to find out the thickness of the band[8]. Within the pulp mill industry the concentration of lye is measured by observing how the laser beam refracts in Laser also works as a spirit level and can be used to indicate a flat surface by just sweeping the laser beam along the surface. This is, for instance, used when making walls at building sites. In the mining industry, laser is used to point out the drilling direction [31, 32].

2.1.2. Environmental Applications

Laser technologies have also been used within environmental areas [33]. One example is the ability to determine from a distance the environmental toxins in a column of smoke [34]. Other examples are being able to predict and measure the existence of photochemical smog and ozone, both at ground level where it isn't wanted and in the upper layers of the atmosphere where it is needed [35]. Laser is also used to supervise wastewater purification[36, 37]. One of these applications is the use of He-Ne infrared laser as source for detection of geometrical dimensions of cracks [38].

2.1.3. Communications

Laser works as a light source in all fiber optics in use [39]. It has greater bandwidth (potentially 100,000 times greater) than an ordinary copper cable. It is insensitive to interference from external electrical and magnetic fields. Crosstalk (hearing someone else's phone call) is of rare occurrence. Fiber optics is used increasingly often in data and telecommunications around the world [40, 41].

2.1.4. Research

Laser has become one of the most important tools to researchers within physics [42], chemistry, biology and medicine throughout the world and is used to: - register ultra-fast chemical processes such as the bonding between atoms to form molecules[43];

2.1.5. Medicine

The use of laser in medication has been established in 1960 and grownup dramatically and common place today [45]. Laser is used in medicine to improve precision work like surgery. Brain surgery is an example of precision surgery that calls for the surgeon to reach the intended area precisely. To make sure of this, lasers are used both to measure and to point in the area in question. Birthmarks, warts and discoloring of the skin can easily be removed with an unfocused laser [46]. The operations are quick and heal quickly and, best of all, they are less painful than ordinary surgery performed with a scalpel. Of greatest interest is the photodynamic laser treatment have shown good results for neck pain [47], bone repair [48],some low risk basal cell carcinoma [49] and non-melanoma skin cancer [50].

2.2. Laser activity of polymer materials

These are not excluded the laser benefit, however there is a limited sources of lasers such as Nd: YAG and Ti: Sapphire, and these materials are very expensive. The

photoluminescence and laser activity of synthetic compounds such as polymer have been investigated [51, 52].

The most important feature of these compounds is the presence of the conjugation of π electrons which is not only involved in their chemically and thermally stabilization. In fact it is responsible from their photophysical properties by playing a major role of HOMO-LUMO interaction and energy transfer in addition to auxochromes attached [54,55].

2.3. Optical Properties of Chalcones

The literature survey has been shown that the laser activity of chalcones is very limited, a crystal of chalcone with two donor auxochromes at para position of ring A and ring B has been studied. It was found that the chalcone is chemically stable and the cutoff wavelength was found to be at 430 nm [56].Sun et al, 2012 have also reported that the compound with such feature has shown a highly fluorescence properties.

The heteroaryl chalcones in different solvents has studies and it was show large red shift in both absorption and emission spectra in polar solvents, the fluorescence quantum yield is mainly depend on the solvents properties [57].

The both of pyrimidine and pyrazole have a lone pair not involved in the π system, this lead to addition electron transfer to that of π system, known as n- π* which also occur at longer wavelength. Pyrimidine is an electron-deficient ring leads to adsorption at shorter wavelengths while pyrazole is a rich one with an opposite properties [58]

The quantum yield to the photoproducts of pyrimidine has been investigated and it was found to be depend on the base auxochromes and phosphate group, phosphate group was shown negative effect, the quantum yield of 0.21 and 0.03 have also reported. The fluorescence of 2-amino-6-hydroxy-4- (3,4-dimethoxyphenyl)-

pyrimidine-5-carbonitrile have been studied and shown the quantum yield ranged 0.0073 to 0.0893 [59]

The complexes of pyrimidine bearing β-ketoiminate ligands have also studied and have shown fluorescence quantum yield higher in solid state than in solution. The reported quantum yield were ranged from 0.55- 0.07 [60]. Whereas the fluorescence properties of biaryl pyrimidine nucleosides were shown quantum yield between 0.152 - 0.001 [61].

SamyA.El-Daly et. al (2013) had been measured the photophysical parameters such as absorption, molar absorptive, oscillator strength, dipole moment, fluorescence spectra, and fluorescence quantum yield of 3-(4-dimethylamino-phenyl)-1-(2,5-dimethyl-furan-3-yl)-propenone (DDFP) in different solvents. They showed that DDFP dye exhibited an essentially larger redshift of the emission spectra than the absorption one as solvent polarity increases. This fact indicates that the dipole moment of the DDFP dye is higher in singlet excited state than that in the ground one [62] .

M. Gaberet.al (2009) were studied the spectral properties of 3-[40-dimethylaminophenyl]-1-(2-pyridyl) prop-2-en-1-one (DMAPP). Cu (II) complexes of were prepared and characterized by elemental analysis as well as spectral studies (IR and UV–vis), ESR, magnetic susceptibilities and thermal studies. The effect of different alcoholic solvents as well as the temperature on the complex formation is studied. The effect of Cu (II) ion on the emission spectrum of the free chalcone is also assigned. The stoichiometry, stability constant, absorption maximum and molar absorptive of the metal complexes as well as the effect of pH, temperature on complex formation are determined spectra photo metrically. Adherence to Beer's law and Ringbom optimum concentration ranges are determined [63] .

The spectral and photo physical properties of two chalcones containing electron donating and accepting groups with intermolecular charge transfer characteristics were synthesized and characterized using ^{1} H NMR, ^{13}C NMR and X-ray crystallography by Mehboobali Pannipara et. Al (2015). Both compounds showed very strong solvent polarity dependent changes in their photophysical characteristics, namely, remarkable red shift in the emission spectra with increasing solvent polarity, large change in Stokes shift, significant reduction in the fluorescence quantum yield; indicating that the fluorescence states of these compounds were of intermolecular charge transfer (ICT) character. The solvent effect on the photophysical parameters such as singlet absorption, molar absorptive, oscillator strength, dipole moment, fluorescence spectra, and fluorescence quantum yield of both compounds have been investigated comprehensively for both dyes.

Anthony synthesized pyrene-containing chalcone derivatives and studied their optical properties in solution and in solid-state. The molecules showed a zero dipole moment at the ground state in contrast to the excited state that exhibited high polar property. The study also revealed that all the molecules were having emission activities that varied according to the substituents appended on the aryl group connected to the carbonyl function of the chalcone. In particular the methoxy functional group greatly contributed to the enhancement of the emission quantum yield in solid-state as compared to the solution [64].

Novel chloroquinoline based chalcones and their derivatives containing 1,2,3-triazole moiety were synthesized and characterized by spectral data and single crystal X-ray crystallography. Their absorbance and emission spectra were investigated and it was observed that compounds having electron withdrawing or halogen substituents on phenyl ring did not show emission. The ground state and excited state dipole moments

of compound were determined using solvate chromic methods. The ground state dipole moment was found to be 1.081 D, while excited state dipole moment was calculated to be in the range of 11.969–3.801 D. Thermal stability was also investigated using thermo gravimetric analysis [65].

3. Theoretical Background

3.1. Introduction

Spectroscopy is a branch of physics where absorption, emission, or scattering of electromagnetic radiation by atoms or molecules, is used to study the behavior of atoms or molecules. In general, the interaction of radiation with matter can cause redirection of the radiation and/or transitions between the energy levels of the atoms or molecules. A transition from a lower level to a higher level with transfer of energy from the radiation field to the atom or molecule called absorption. A transition from a higher level to a lower level called emission if energy transferred to the radiation field or nonradioactive decay if no radiation is emitted as shown in (**Fig 3.1**). Redirection of light due to its interaction with matter called scattering, and may or may not occur with transfer of energy, i.e., the scattered radiation has a slightly different or the same wavelength [66-71].
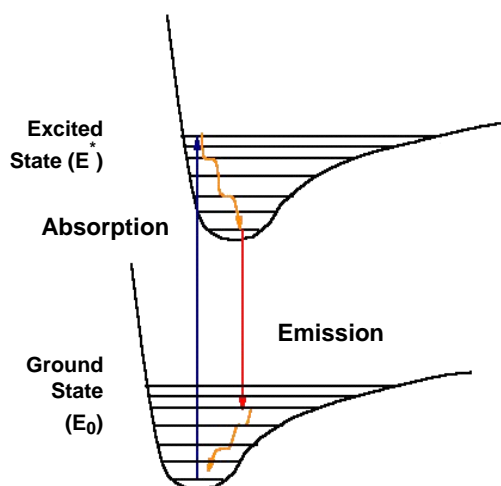
Fig 3.1 Transition between molecular electronic energy levels.

When a molecule absorbs a photon, it gains an excess of energy, becomes energetically unstable relative to the ground state and called excited molecule (it enters an electronic excited state). To get the formation of an electronically excited state, a molecule must absorb a photon of radiation with energy that is equal to the difference between the excited and the ground state [72] .

The energy of the absorbance photon [72]:

$$E = h\nu = (E_{excited}) - (E_{ground}) \tag{3.1}$$

Where, h and ν are the Planck's constant and the frequency of radiation respectively.

Since absorption of radiation of much longer wavelengths induces vibrational and rotational excitation of the molecules ground electronic state, the energy of this electronic excited state defined as the energy difference between the vibrational levels of quantum number zero of the two states as shown in (**Fig 3.2**). For most molecules, this corresponds to radiation in the ultraviolet and visible wavelength region (200-700 nm) of the electromagnetic spectrum [73].
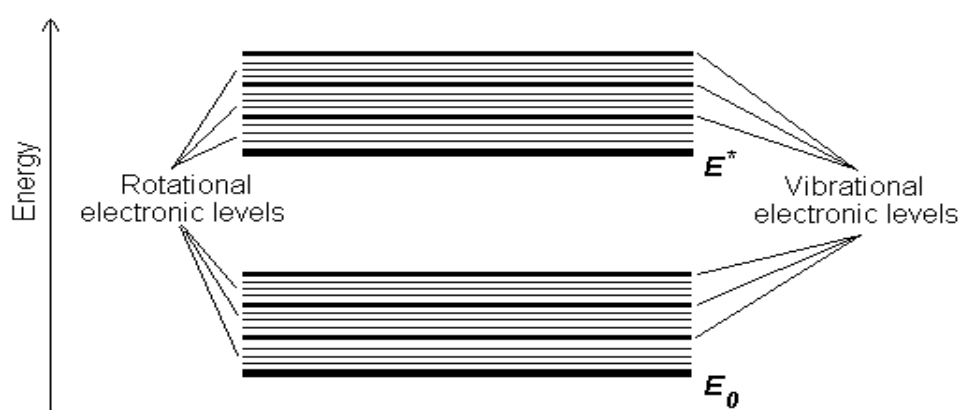
Fig 3.2 Shows the electronic rotational and vibrational levels.

The electronic states of most organic molecules can divide into singlet states (S) and triplet states (T). These terms are determined from the spin multiplicity of the electronic excited state, which derived from the spin angular momentum of the electrons in the state. Two electrons said to be spin paired if their spins are antiparallel, one up and one down, the resultant total angular momentum (S) is zero. Therefore, the spin multiplicity is unity and a singlet state. If however, the two unpaired electrons have their spins parallel, both spin up or both spin down, then the resultant total angular momentum (S) is one, the spin multiplicity will be three, and this said to be a triplet state as shown in **Fig 3.3** [74]

	Ground	Excited	Excited

Ground
Singlet state

Excited
Singlet state

Excited
Triplet state
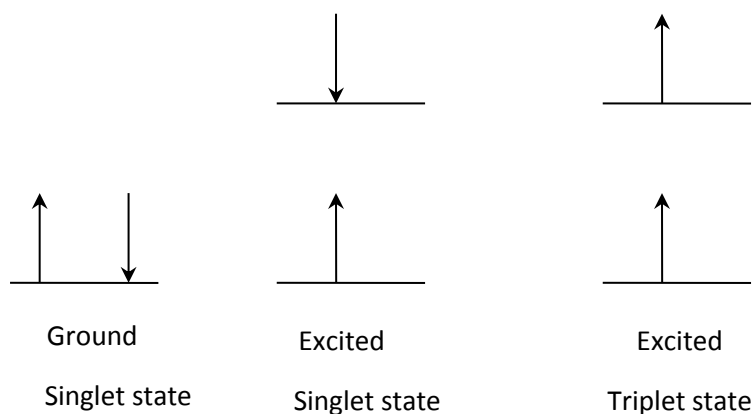
Fig 3.3 Shows the singlet and triplet states.

The promotion of electrons from the highest to the lowest unoccupied molecular orbital occurs without change in the total spin, and is characterized by the strongest band in the absorption spectrum; that of the $S_0 \rightarrow S_1$ transition. The $S_0 \rightarrow T_1$ transition has a very low probability of occurring and said to be spinning forbidden. However, through the phenomenon of spin-orbit coupling it is possible for the triplet states to reach from singlet states [75].

3.2. The Absorption

When atoms or molecules absorb light, the incoming energy excites them to higher energy level. This type of electronic transition called electronic absorption or electronic excitation. The speed of light is $c=3\times10^{8}$m/sec, the frequency of oscillation of the electric and magnetic field or the frequency of the light is ν, the wavelength of the light is λ these properties of the light related by the following equation [72]:

$$C = \lambda \nu \qquad (3.2)$$

In addition, the energy of the radiation is:

$$E = h\nu = \frac{hc}{\lambda} \qquad (3.3)$$

Where, h is Planck's constant ($h=6.625\times10^{-34}$J.sec). A necessary condition for light of frequency ν to be absorbed by a molecule in its ground state is that the energy gap between the ground state and excited state to which excitation occurs is exactly equal to $h\nu$, as mentioned in equation 3.1. Therefore, the type of excitation depends on the wavelength of the light. Electrons promoted to higher orbitals by ultraviolet or visible light; vibrations excited by infrared light and rotations excited by microwaves radiation [75].

An absorption spectrum is the absorption of light as a function of wavelength. The spectrum of an atom or molecule depends on its energy level structure, and absorption spectra are useful for identifying of compounds. Because the distribution of molecular electronic charge (i.e. the dipole moment) changes when light is absorbed, the absorption of light by a molecule also called an electronic dipole transition. The dipole moments associated with the various electronically excited states of a molecule are generally different. The line along which the resultant dipole moment changes on

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going from the ground state to any given excited state called the direction of polarization of the electronic transition[76]. The electronic transition in which we are interested here (n→π*, π→π*). The intermolecular charge transfer transition of aromatic molecules is all affected by light of 200-700 nm [76].

The electronic absorption spectrum of a molecule is a graphical representation of the intensity of light absorbed in producing electronic transitions in the molecule, as a function of the frequency (or wavelength) of the light. In regions where the intensity of light absorbed is high are said to occur strong absorption bands. In regions of frequency where the intensity of light absorbed is low, weak absorption bands occur. Although most absorption spectra are represented as absorbance or absorption intensity vs. wavelength, a proper absorption spectrum represents absorbance vs. frequency because the frequency is linearly related to the energy gaps between the states involved in the electronic transitions that form the bases of the spectral bands while the wavelength is hyperbolically related to frequency and energy [76] .

Aromatic molecules having n-electrons on atoms participating in the aromatic structure may show n→π bands at lower frequencies more than any of the n →π*bands. This is a result of the n-orbitals in the ground state of the molecule being higher in energy than the occupied π-orbitals. n and π*bands are usually ten to one hundred times weaker than the 1_{La} or 1_{Lb} (the singlet excited states of high orbital angular momentum) bands because the n-orbitals are directed at right angles to the π*-orbitals while the π andπ*-orbitals are parallel or collinear. This results in poorer orbital overlap between the n-and π*-orbitals than between the πandπ*-orbitals and make for lower transition efficiency in n →π* promotion. The theoretical treatment of the intensities of absorption bands was behind our scope. However, experimentally found that by the Lambert – Beer law [77]:

$$\left(\frac{I}{I_0}\right) = 10^{-\epsilon cl} \qquad\qquad (3.4)$$

In which I and I_0 are the intensities of light transmitted through the absorber and incident upon the absorber, respectively. Moreover, ϵ, c and ℓ are molar absorptivity, the concentration of absorbing molecule in the sample and the length of the path of light through the sample respectively. I / I_0 represent the fraction of light waves of the proper frequency to produce the electronic transition, absorbed on passage through the sample. For chemical purposes (3.4) is usually represented in logarithmic form [78]:

$$A = \log\left(\frac{I_0}{I}\right) = \epsilon c\ell \qquad\qquad (3.5)$$

In which A called the absorbance or optical density of the sample. Measuring the concentration of absorbing species in a sample is accomplished by applying the Beer-Lambert Law.

Molecular electronic absorption spectral bands are not thin lines occurring at one frequency as (3.1) might imply. Rather, they are spread over several thousands of wave numbers (wave numbers are expedient frequency units equivalent to reciprocal wavelength in cm) and may appear featureless and bell shaped or may demonstrate clear or at least discernable fine structure (i.e. several closely spaced peaks may appear in one spectral band). The breadth and fine structure of molecular electronic absorption bands are results of the dependence of atomic motions (vibrations) in the molecule upon the changes in charge distributions produced by electronic transition [77].

In rigid aromatic ring molecules and in certain aromatics containing functional groups, vibrational substructure generally quite pronounced in absorption spectra [79].

Absorption of UV radiation by a molecule excites it from a vibrational level in the electronic ground state to one of the many vibrational levels in the electronic excited state. This excited state is usually the first excited singlet state. A molecule in a high

vibrational level of the excited state will quickly fall to the lowest vibrational level of this state by losing energy to other molecules through collision. The molecule will also partition the excess energy to other possible modes of vibration and rotation. Molecules that are excited to high energy levels can decay to lower levels by emitting radiation, This process called emission or luminescence. In other word, luminescence is the emission of photons from electronically excited states. Luminescence divided into two types depending on the nature of the ground and the excited states. In a singlet excited state, the electron in the higher-energy orbital has the opposite spin orientation as the second electron in the lower orbital. These two electrons called paired. In a triplet state, these electrons are unpaired, that is, their spins have the same orientation. Return to the ground state from an excited singlet state does not require an electron to change its spin orientation. The changing in spin orientation is need for a triplet state to return to the singlet ground state [76].

3.3. The Fluorescence

The phenomenon, Fluorescence of substances, had been observed for hundreds of years and was explained by the British scientist Sir George G. Stokes in (1852) that fluorescence can be induced in certain substances by illuminated with ultraviolet light. He formulated Stoker's law, which states that the wavelength of the fluorescent light is always greater than that of the exciting radiation; therefore, fluorescence is the phenomenon in which absorption of light of a given wavelength by a fluorescent molecule followed by the emission of light at longer wavelengths. Therefore, fluorescence is the emission that results from the return to the lower orbital of the paired electron. Such transitions are quantum mechanically "allowed" and the emissive rates are typically near $10^8 sec^{-1}$. These high emissive rates result in fluorescence lifetimes

near 10^{-8}sec or 10 *n sec*. The lifetime is the average period of time a fluorescence remains in the excited state [72].

Phosphorescence is the emission that results from transition between states of different multiplicity, generally a triplet excited state returning to a singlet ground state. Such transitions not allowed and the emissive rates are slow. Typical phosphorescent lifetimes range from milliseconds to seconds, depending primarily upon the importance of deactivation processes other than emission as shown in (**Fig 3.4**).
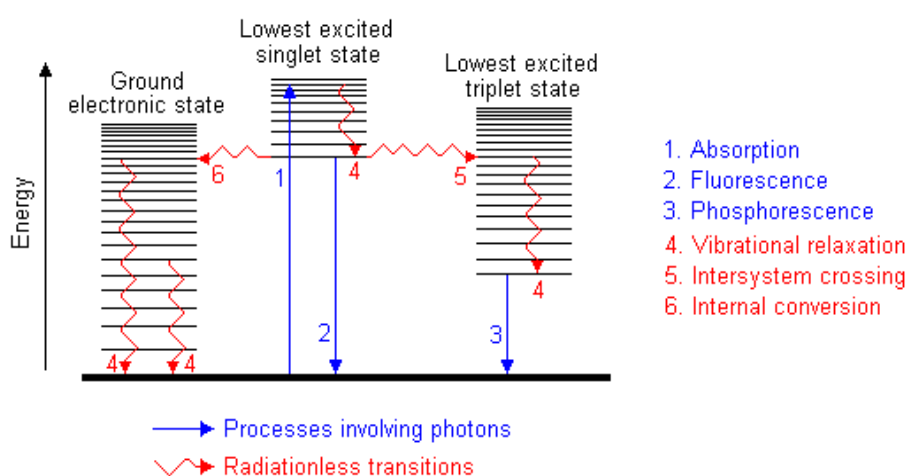
Fig 3.4 Possible physical process following absorption of a photon by a molecule.

For atoms excited by a high-temperature energy source, this light emission commonly called atomic or optical emission. For molecules, it called fluorescence if the transition is between states of the same spin and phosphorescence if the transition occurs between states of different spin. The emission intensity of an emitting substance is linearly proportional to analytic concentration at low concentrations, and is useful for quantitating emitting species [77].

(**Fig 3.5**) shows how incident radiation excites the ground singlet state molecule S_o into an excited singlet state S_1. In addition to this, the molecule is also excited into vibrational levels of the singlet excited state. These rapidly undergo radiation less

deactivation, induced by collisions with surrounding media, until the molecule reaches its lowest excited singlet state in femto – pico seconds. The molecule may then undergo two processes; it may be completely deactivated by the solvent; or, may fluoresce in pico – nano seconds [77].

There are some factors controls the occurrence of fluorescence. Where the interaction between excited molecules and surroundings is strong, radiation less decay will predominate. But, if the interaction between them is ineffective at achieving the large energy, transfer needed to take the molecule to a lower electronic state. The radiative decay dominates and the molecule fluoresces. The fluorescence will show in two important characteristics. First, fluorescence may appear as an approximate mirror image of the absorption at a lower energy, and hence lower frequency (longer wavelength) than the absorption, the difference (in wave numbers) between the two corresponding bands being known as the Stokes shift. Second, fluorescence emission may show vibrational structure which can provide information about the force constants of the molecule in its ground state (the electronic structure provides information about the vibrational relaxation in the higher excited states is so rapid that emission cannot complete with radiation less deactivation of the upper states as shown in (**Fig 3.5**). Where upon fluorescence only occurs from the lowest excited singlet state to the ground state. The presence of more than one fluorescence band in the fluorescence spectrum of a molecule is indicative that fluorescence is occurring from more than one chemical species. Most often, impurities account for extraneous fluorescence bands. Because other processes like intersystem crossing and internal conversion compete with fluorescence for deactivation of the lowest excited singlet state, of a given number of molecules in the lowest vibrational level of their lowest excited singlet state at any

instant of time, not all will return to the ground state by fluorescence [66].force constants in the excited state) [80].

Fluorescence can provide information about the lifetime and the energy of the excited singlet state. Nearly all compounds absorb UV or Visible light, but only a few will fluoresce. Most fluorescent organic compounds contain aromatic rings, but not all aromatic compounds fluoresce [76, 77, 79, 81, 82].

Although, corresponding to several transitions, the electronic absorption spectrum of a molecule may contain several absorption bands. From the ground state to the various excited singlet states, the fluorescence spectrum will invariably show only one emission band, even if higher frequency absorption is excited, because internal conversion and

3.4. Quantum Yield of Fluorescence

The fraction of excited molecules that do fluoresce called the quantum yield of fluorescence (Φ_F), or fluorescence efficiency. It is a physical constant of the excited molecular species. In terms of the rates of processes competing for deactivation of the lowest excited singlet state, Φ_F is given by [66, 83, 84]:

$$\Phi_F = \frac{K_F}{K_F + \sum K_D} \qquad (3.6)$$

Where K_F is the molecular probability of the excited molecule will fluoresce (rate constant for fluorescence) and ΣK_D is the sum of the rate constants for deactivation of the lowest excited singlet state by all competitive radiation less processes (for isolated molecules, ΣK_D is the sum of the rate constants for internal conversion and intersystem crossing) [1]. With the greater number and greater rates of radiation less processes, the Φ_F will be small. The quantum yield of fluorescence usually decreases with increasing temperature. This is a result of the population of higher vibrational levels of the lowest excited singlet state, by increased temperature, which contributes to the increase in ΣK_D and the deactivation of the excited state by vibrational (non-radiative) pathways.

The radiative lifetime of the lowest excited singlet state is $t_0 = K_F^{-1}$. The excited molecule would spend this mean time in the excited state if fluorescence were the only means of deactivation of the excited state [85].

The lifetime of the lowest excited singlet state is $t_1 = (K_F + \Sigma K_D)^{-1}$. In addition, corresponds to the actual mean time the molecule spends in the excited state. The quantum yield of fluorescence maybe expressed in the following [66].

$$\Phi_F = \frac{t_1}{t_2} \tag{3.7}$$

Since (Φ_F) is a fraction (never greater than 1), t_0 is always greater than or equal to t_1. In general, the greater number of processes competing with fluorescence for deactivation of the lowest excited singlet state and the greater their rate constants the shorter will be the actual lifetime of the lowest excited singlet state. Molecules having heavy atoms or non-bonded electron pairs usually have high rates of intersystem crossing. Moreover, molecules having an n, π * state as the lowest excited singlet state have long radiative lifetimes as a result, intersystem crossing is usually 100 percent effective in deactivating the lowest excited singlet states of molecules giving lowest, n, π * excited states, and fluorescence is very rarely observed from these molecules [86].

The relationship between fluorescence intensity and molecular related to the transition can be obtained from the Lambert-Beer law. From (3.4) $I/I_0 = 10^{-\varepsilon c \ell}$ is the fraction of light intensity transmitted in exciting a transition whose decades molar extinction coefficient is ε at wavelength of excitation in a sample whose molar concentration is c, and has an optical path length ℓ in cm, then the fraction of light absorbed is[86] :

$$(I_a / I_o) = 1 - (I / I_o) = (I_o - I) / I_o = 1 - 10^{-\varepsilon c \ell} \tag{3.8}$$

However, if the fluorescence has a quantum yield Φ_F, fraction of the absorbed light which appears as fluorescence (I_F / I_a) is [86]:

$$(I_F/ I_o) = \Phi_F (I_a/ I_o) = \Phi_F (1 - 10^{-\varepsilon c \ell}) \tag{3.9}$$

Or in arbitrary units, the intensity of light emitted is [86]:

$$I_F = \Phi_F I_o(1 - 10^{-\epsilon Cl}) \tag{3.10}$$

The term $(1 - 10^{-\epsilon Cl})$ can be expanded in a power series if ϵcl is very small, would reduces to [86]:

$$(1 - 10^{-\epsilon Cl}) = 2.3 \epsilon cl \tag{3.11}$$

Thus, in the limit of low absorber concentration [86]:

$$I_F = 2.3\ \Phi_F I_o \epsilon cl \tag{3.12}$$

It can be seen then, that on a molecular basis, I_F depends upon the concentration and molar absorptive of the absorbing (ground state) species and the quantum yield of fluorescence, a property of the fluorescing (excited) species. For analytical purposes, 3.12 has too many factors to determine to be useful. However, under conditions of constant excitation, Φ_F I_o, ε and ℓ are the same for unknown and standard samples, and relative fluorometry can employ by dividing 3.12 for the unknown sample by 3.12 for the standard sample for the same molecule [86].

$$\frac{I_{FU}}{I_{FS}} = \frac{c_U}{c_S} \tag{3.13}$$

Where I_{FU}, I_{FS}, c_U and c_S are the experimentally determined fluorescence intensities of unknown, standard samples, the concentrations of fluorescing material in unknown and in standard samples, respectively [77, 79, 86].

Fluorescence detection has three major advantages over other light-based investigation methods: high sensitivity, high speed, and nondestructive. Sensitivity is an important issue because the fluorescence signal is proportional to the concentration of the substance investigated. Relatively small changes in ion concentration in living cells can have significant physiological effects. Whereas absorbance measurements can reliably determine concentrations only as low as several tenths of a micro molar, fluorescence

techniques can accurately measure concentrations one million times smaller and even femto molar [77, 79, 81].

3.5. The Fluorescence Lifetime

Life times are frequently used in describing transitions between different states. The time during which the number of atoms in a given excited state diminishes to $\left(1/e\right)$ of its initial value is called lifetime of the excited state as shown in (**Fig 3.5**). The lifetime determined in this way coincide with the average time spent by atoms in the excited state [81].

Suppose an atom is in an excited state E_2. Let the probability that the atom will leave that state in time dt be ρdt. Therefore, if N_2 is the number of atoms in state E_2 at any time t, [81]

$$\frac{dN_2}{dt} = -N_2\rho \tag{3.14}$$

Integrating this equation, we have

$$N_2 = -\rho t + const \tag{3.15}$$

$$N_2 = N_{20} \, at \, t = 0 \tag{3.16}$$

$$N_2 = N_{20}e^{-\rho t} \tag{3.17}$$

The average lifetime of an atoms in the state E_2 is

$$\tau = \frac{1}{N_{20}} \int t\rho N_{20}e^{-\rho t} dt = \frac{1}{\rho} \tag{3.18}$$

$$\text{So } A_{21} = \frac{1}{\tau} \tag{3.19}$$
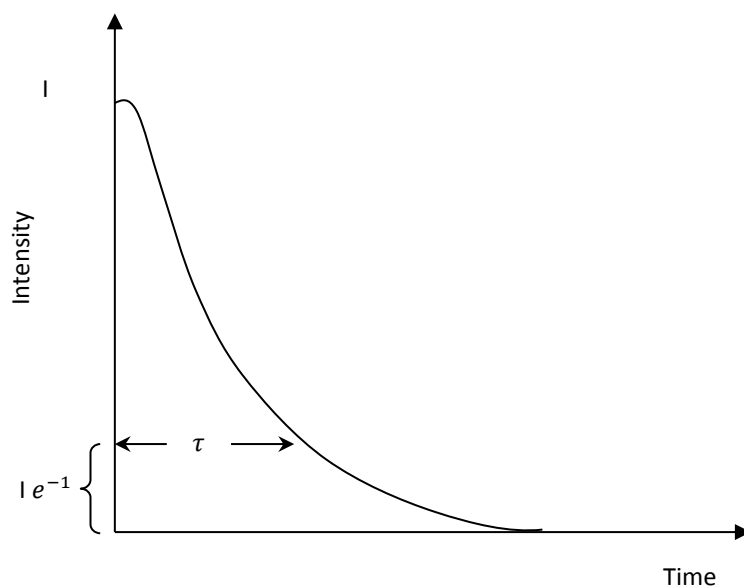
Fig 3.5 Decay of an excited state

3.6. The Stokes Shift

When a system (of molecules or atoms) absorbs a photon, it gains energy and enters an excited state. One way for the system to relax is to emit a photon, thus losing its energy (another method would be the loss of heat energy). When the emitted photon has less energy than the absorbed photon, this energy difference is known as the Stokes shift as shown in (**Fig 3.6**).
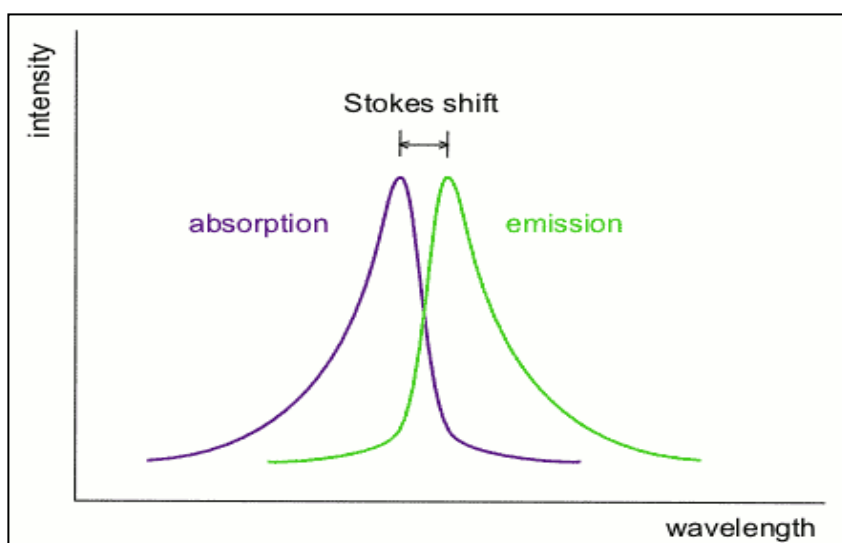
Fig 3.6 Stokes Shift

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Lippert and Mataga [87-89]had shown that the Stokes shift has a linear variation with the dipole factor, given within square brackets in the expression [87-89]:

$$\nu_a - \nu_f \approx \left[\frac{(D-1)}{(D+1)} - \frac{(n^2-1)}{(n^2+1)} \right] \frac{(\mu_e - \mu_g)^2}{a^3 hc} \qquad (3.20)$$

$$\text{Dipole factor} = D_f = \left[\frac{(D-1)}{(D+1)} - \frac{(n^2-1)}{(n^2+1)} \right] \qquad (3.21)$$

Where, ν_a and ν_f are absorption and fluorescence peaks in wave numbers, D the dielectric constant and "n" the refractive index of the solvents, μ_e and μ_g represent the dipole moment of the solute in the excited state and the ground state respectively, and 'a' is the radius of the solvent cage around the solute.

3.7. Dimer

When an organic molecule in ground state combine with another molecule also in ground state a dimer is formed. This can be identified by a weak band in the long wavelength side of absorption band of monomer. Most often, the dimers are quenchers of fluorescence and hence laser action [90].

3.8. Excimer

Excimers are complex electronically excited molecules with molecules of the same species in their ground state. They exist only in the excited state and they dissociate into monomers upon radiative or radiation less deactivation. Since, the emitting species is bimolecular with one in the excited state and other in the ground state it's called "Excited State Dimer" or short word Excimer [90].

Excimers have been studied by many research groups and the results have been summarized by Foster and Birks [90]. Excimer means, only one molecule in high excited state combines with other molecule still in the ground state. This can be schematically represented as: [87]

$$A \xrightarrow{h\nu} A^* \qquad\qquad\qquad (3.22)$$

$$A^* + A \rightarrow A^*A \qquad\qquad\qquad (3.23)$$

Where: A : *Molecule in the ground state.*

A^* : *Same molecule in the excited state.*

The most prominent feature of Excimer is the broad and structure less fluorescence band which is shifted 5000-6000cm^{-1} to lower frequencies relative to the molecular fluorescence. This fluorescence can be observed in liquid solution and, also in solids, if the crystal structure allows a close overlap of the molecular planes. Absence of excimer emission at room temperature does not ensure the absence of excimer formation, because a small enthalpy of formation may lead to rapid dissociation. If the lifetime of the excited monomer is short, fairly high concentrations are needed in order to observe the formation of the excimer. The concentration quenching of fluorescence is often due to excimer formation, followed in some cases (e.g. in anthracite) by a photochemical reaction [87].

Since the formation of excimer in solution is diffusion controlled, the viscosity of the solvent plays an important role. Increasing the temperature therefore favors association, but at high temperature the situation is reversed and thermal dissociation to excited and non-excited monomers predominates. If the temperature is so high that dissociation and association are rapid compared to the deactivation process, equilibrium between excimer and excited monomer is established, which leads to a common exponential decay of excited monomer and excimer emission. At low temperature, on the other hand, when excimer dissociation is negligible, two exponential decays are observed. In the transition range the decay is non-exponential [90].

The experimental studies have shown that the capability of forming excimers is common to most planner aromatic molecules. The nature of this unusual kind of molecular bonding is therefore of great interest for an understanding of photophysics and photochemical processes in aromatic compounds. The first theoretical approaches were based on charge resonance and excitation resonance interaction. Since neither of these models of configuration interaction between charge resonance and excitation resonance states has been established an alternative treatment considers the excimer as a "super molecule". The excimer theories have recently reviewed by Birks [90].

3.9. Exciplex

Similar to excimer, in which both molecules belong to same or a very similar chemical species, excited complexes, can be formed from chemically different molecules and these also dissociate into monomers after deactivation. These complexes are called hetero-excimer or exciplexes. Since excitation resonance is possible in exciplexes, because of the different energy levels of constituents, charge transfer (CT) provides the binding energy. The difference (I − A) between donor ionization energy I and the acceptor electron affinity A is therefore a decisive criterion. If this difference is too small, ground state (CT) complexes are formed. Exciplex often show fluorescence which depends much more critically on polarity of the solvent than does excimer fluorescence. Here the mechanism is schematically given as: [90]

$$A \xrightarrow{h\nu} A^* \qquad\qquad (3.24)$$

$$A^* + B \rightarrow A^*B \qquad\qquad (3.25)$$

Where: A^* : Molecule in the excited state.

A : Same molecule in the ground state.

B : Another molecule in the ground state.

3.10. Dye Photophysics

Laser dyes typically show large absorptivities, as measured by their molar extinction coefficients, ϵ(units of liter/mole cm^{-1} or M^{-1} cm^{-1}). This feature responsible for high optical densities associated with moderate concentration $(10^{-4} - 10^{-5}M)$of dye and results from the high degree of delocalization and polarizability of π electrons in dye structure [91].

The degree to which electron density in a dye molecule is "rearranged" or polarized as the result of absorption of photon is related to transition dipole moment or oscillator strength (f) for the electronic transition. The parameter f is related to first approximation, using classical theory, to the extinction coefficient (ϵ) [91].

$$f = 4.3 \times 10^{-9} \int \epsilon. \, d\nu = 4.3 \times 10^{-9} \epsilon_{max} \Delta \nu_{1/2} \qquad (3.26)$$

Where ϵ is the experimental extinction coefficient andν is the energy (in wave numbers) of absorption in question. The integral of ϵ is more conveniently approximated by product of extinction coefficient at absorption maximum and width of absorption band at $\frac{1}{2}\epsilon_{max}$(Eq.3.18). The importance of oscillator strength is underscored on noting the relationship between f and rate constant for radiative decay of an excited dye molecule (hereK_f, the rate constant for fluorescence emission) [91].

$$K_f = (\nu_m)^2 \qquad (3.27)$$

where (ν_m) is the energy corresponding to maximum wavelength of absorption The probabilities of both spontaneous emission (as reflected in K$_f$) and stimulated emission (the latter responsible for "gain" or light amplification in dye laser cavity) are related to the size of the transition moment and oscillator strength in the same way[92].

The most important electronic energy levels for organic dyes in fluid media are the ground state (S$_0$) and the electronic excited state (S$_1$). The absorption of light which

raises molecules to upper level is associated with promotion of an electron in a bonding orbital to ant bonding (virtual) orbital of the molecule. This electronic rearrangement is accompanied by a displacement of the equilibrium nuclear coordinates of the molecule; the vibrational energy states associated with these nuclear coordinate changes are depicted by sub-spacing's [93].

Thus, the dye laser may be viewed as a four- level system in the most probable excitations proceed to populate upper vibrational levels in S_1, a vibrational relaxation to the "zeroth" level in S_1 follows, and emission occurs to repopulate an upper vibrational level of ground state S_0 [93].

Sauers et al [94] have noted that the most common dyes are not optimally designed for laser action with respect to the shaping of the absorption-emission bands of organic dyes which are broadened due to vibrational (rotational) relaxation[94]. They reason that absorption and emission strength associated with $0 - 0$ transitions*(i.e. from zero vibrational level of S_0 electronic level to zero vibrational level of S_1 electronic level)* for which the probability of stimulated emission (to the overpopulated lowest ground state) is low [94]. The absorption and emission spectra for the well-known xanthene dye, rhodamine B, with the reference to the position of the peak lasing wavelength. Rutgers [95] group further proposes that the "shaping" of spectral bands in favor of the "satellites" corresponding to $0 - 1$ or $0 - 2$ transitions can be predicted for synthetically attainable structures. The approach was illustrated with the xanthenone ("rhodamine") dye, for which a slightly higher lasing output in the satellite region (559nm) was observed. [94] The process of dye fluorescence (K_f) must complete with nonreactive decay of excited species by internal conversion to the ground state (K_d) [94].

3.11. Theory of Amplified Spontaneous Emission (ASE)

We shall now consider the concept of amplified spontaneous emission (ASE). Consider the situation in (**Fig 3.7**), with an amplifier being pumped by an external source. Although no externally injected signal is shown there, the atoms in excited state still radiate spontaneously into the frequency interval that matches the gain profile of the remaining part of the amplifier [96].

Let us focus on the radiation $I^+(v, z)$ travelling in the positive z direction and contained within a constant solid angle $d\Omega/4\pi$. The atoms in N_2 at z = 0 radiate part of their energy spontaneously into this solid angle; and this radiation, in turn, is amplified by the inversion between z = 0 and z = ℓ. Thus spontaneous emission is continuously added to I^+ along z, and, simultaneously, stimulated emission amplifies the power from previous lengths. (It's important to note that, this is an incoherent radiation, and thus power rather than fields must be added.) [96].

Then

$$\frac{d}{dz} = [I^+(v,l)dz]Y_0(v)I^+(v,z)dv + hvA_{21}N_2g(v)dv\left(\frac{d\Omega}{4\pi}\right) \qquad (3.28)$$
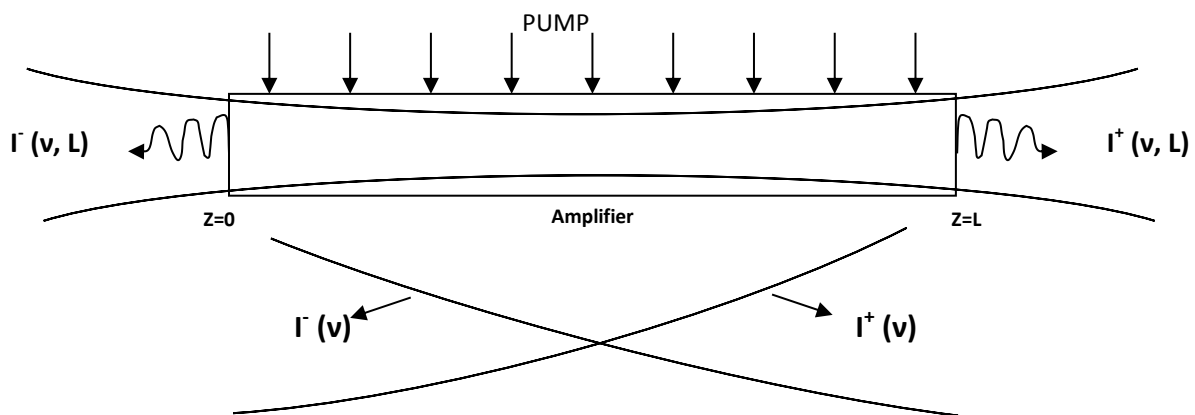
Fig 3.7 Optical amplifier generating broad band incoherent radiation

A solution to this linear first order differential equation subject to the boundary

condition that $I^+(v, z = 0) = 0$ is readily obtained: [96]

$$I^+(v, z = 1) = \frac{hvA_{21}N_2g(v)}{Y_0}\,(e^{Y_0(v_0)}-1)(d\Omega/4\pi) \qquad (3.29)$$

gain coefficient $\gamma_0(v)$ to the population inversion absorption coefficient, we

obtain a very important formula:[96]

$$I^+(v, l) = \frac{8\pi n^2 hv^3}{c^2}\frac{N_2}{N_2-(g_2/g_1)N_1}[G_0(v) - 1](d\Omega/4\pi) \qquad (3.30)$$

where $G_0(v) = e^{Y_o(v)l}$ is the small gain of amplifier. (This formula applies

equally well to an absorptive system with $N_2 < \left(\frac{g_2}{g_1}\right)N_1$ and $G_0 < 1$ (i.e., the cell is an

attenuator).

Equation (3.30) is very important and it's worthwhile to digress for a moment to

appreciate its significance [96].

3.11.1. An optically "Thin" Amplifier or Attenuator

If $G_0(v)$ is very close to 1, the amplifier (or attenuator) is said to be

optically thin, and thus $(Y_0(v)l)$ is small. [96] Therefore the Taylor series expansion of

$e^{Y_o(v)l} - 1$ yields $Y_o(v)l$, and we obtain :[96]

$$I^+(v, l) = hvA_{21}N_2g(v)\left(d\Omega/4\pi\right) \qquad (3.31)$$

This states that the power from $N_2 l$ atoms radiating into $d\Omega/4\pi$ as $g(v)$ add their

radiation. In other words, each element dz along z contributes as equal amount to the

power [96].

3.11.2. A thermal population

If the atomic populations are such that $N_2 < \left(\frac{g_2}{g_1}\right)N_1$, the amplifier is an

attenuator and $G_0 < 1$ Furthermore, if N_2/N_1 can be related to a "temperature" by

Boltzman relation [96]

$$\frac{N_2}{N_1} = \frac{g_2}{g_1}Exp\left[-\frac{hv}{KT}\right] \qquad (3.32)$$

Then (3.30) becomes [97]

$$I^+ = (v, l) = \frac{8\pi n^2 h v^3}{c^2} \frac{1}{Exp\left(\frac{hv}{KT}\right)-1} \left[1 - e^{-|Y_0(v)|l}\right](d\Omega/4\pi) \qquad (3.33)$$

We could immediately recognize the quantity in the brackets as Planck formula for black body radiation for, $I(v) = \left(\frac{c}{n}\right)\rho(v)$. The remaining factor $1 - e^{-Y_0 l}$ is a measure of black body power available to the out side world. Its maximum value is, of course, unity for an optically thick medium (i.e., $e^{-Y_0 l} \ll 1$) [96].

Thus we see that the quantity in parentheses in (3.33) is the emissivity of the system for a normal population ratio. Since the factor $1 - e^{-Y_0 l}$ is also the absorption of a wave passing through the attenuator, we have thus derived Kirchoff's radiation law which states that a body can emit only as much black body radiation at a frequency v as it can absorb [96].

If the lower state population increases with z, as it does, for instance, in a high pressure sodium lamp (with z treated as the radius), the central part of the spontaneous emission is heavily attenuated, whereas the wigs escape more or less unimpeded. Under such circumstances we can easily obtain a self-reversed line [96].

Let us now consider some of the consequences of (3.30). First, we should remind ourselves that it was derived under the assumption that the population N_2 and N_1 were not saturated by stimulated emission. Under such circumstances and high gain, the spectral width of the amplified spontaneous emission is narrow than that predicted by the line shape g(v) as given, for instance, by (3.31) [96].

A few numbers should convince us of this fact. Suppose that $G_0(v_0)$ (i.e., the gain at line center) were 100. then the factor $G_0(v_0) - 1 = 99$.

At $v = v_0 \pm \Delta v/2$, $\gamma(v) = \gamma_0(v_0)/2$, $G_0(v) = [G_0(v_0)]^{1/2} = 10$. Thus this factor is now equal to 9, a reduction by factor of 11 in changing the frequency by a mere $\Delta v/2$. Thus spectral narrowing is to be expected from a system with high gain as shown in (**Fig 3.8**).

Here, spectral narrowing has been shown for different gain [96].
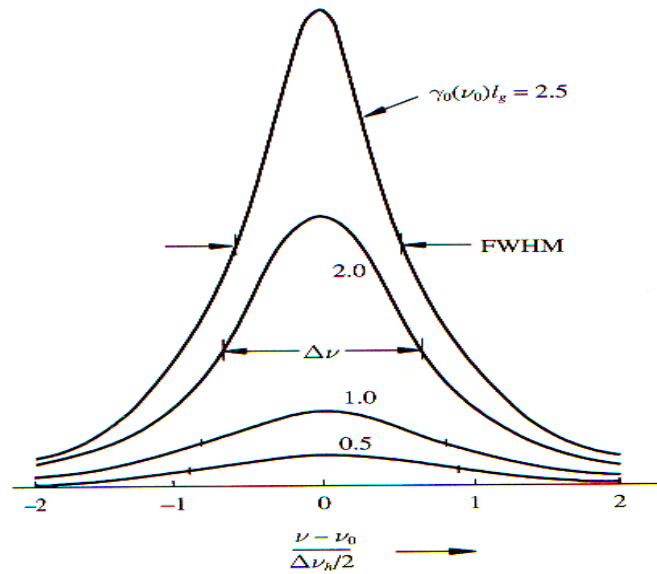
Fig 3.8 Spectral narrowing of spontaneous emission in an unsaturated amplifier

We cannot carry this analysis to the extreme of letting the intensity become

Arbitrarily large. If the line is in homogenously broadened, then too large intensity at line center will burn a hole at line center but leave the wigs unaffected. When this happens, the line width begins to expand back toward its optically thin value different; equation (3.28) used the small signal gain coefficient, whereas now one would need to include saturation [96].

It's important to note that above consideration is true only when the intensity of ASE is not too high, otherwise, saturation would set in and broaden the spectra profile. Then under non saturation condition, ASE of a high gain laser produces quite collimated (divergence 10 m rad), intense and spectrally narrow light ($\Delta\lambda = 5nm$) [96].

This ASE is more coherent than thermal light, but less coherent than a conventional lasers with resonators. Dye laser, excimer laser and N_2 laser are good example of lasers working in ASE mode. If the amplified spontaneous emission (ASE)

saturates the population inversion, that inversion energy cannot be extracted by an externally injected coherent laser signal. Thus the curse of ASE is that limits the maximum gain that can be built into an amplifier [96].

3.12. Laser Structures

The key features of a laser are a material that amplifies light (known as the gain medium) and a resonator that applies feedback36. As light passes through the gain medium, it stimulates the emission of more light, thereby gaining intensity. The resonator reflects the light backward and forward through the gain medium to build up a very intense light field. A very important point is that the additional light stimulated has the same wavelength, direction, and phase as the light passing through the gain medium, which leads to the distinctive coherence properties of laser light, e.g. being collimated in a narrow beam and (usually) monochromatic. Energy must be supplied to a laser in order for it to operate, and there are two main ways of doing this. The first, known as optical pumping, is to excite the gain medium with a powerful light source. This would normally be either another laser or a flash lamp. The other possibility, electrical pumping, involves exciting the gain medium electrically by passing a current through it. In all lasers there is a minimum pumping rate or energy, known as the threshold, which must be supplied in order for lasing to occur [98].

3.13. Dye Laser Pumping Techniques

A wide range of optical pumping and resonator schemes are possible for organic dye lasers. The high optical power densities achievable from laser sources make them ideal for optically pumping organic dyes. However, the spatial coherence of the laser source allows a more precise control over the optical pumping geometry than is possible from incoherent flash lamp.

When the laser used as pumping source, we have longitudinal and transverse pumping schemes. A longitudinal pumping schemes typically used with continuous wave (CW) dye laser is shown in (**Fig 3.9**) An Argon ion laser is focused by mirror M_1 to the small spot in dye cell [98]

Transverse optical pumping is achieved typically by using a cylindrical lens to focus a laser beam into a narrow strip. The narrow strip of radiation is then directed on the dye cell and the laser action takes place along the strip transverse to the pumping radiation. (**Fig 3.10**) shows transverse pumping.

If we use flash lamp, the flash lamp should be capable of reaching its peak power in about 1μsec or less. This is important since the Upper Laser Level (ULL) lifetime in dyes is about 5 ns and the transfer of excited molecules from S_0 to T_1 is quite fast. This makes the linear flash lamp better suited for flash lamp pumped dye lasers; because linear flash lamp has a small inductance and fast rise time of current pulse.

In addition dye circulation and chemical quenching of triplet rate effect is essential. The flash lamp pumped dyes lasers are capable of giving 1J energy per pulse [98].
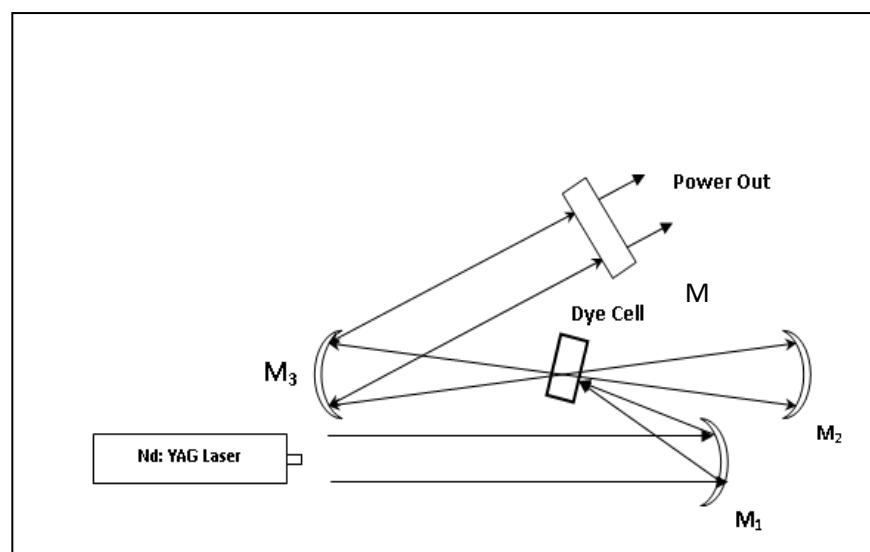
Fig.3.9 Longitudinal pumping system
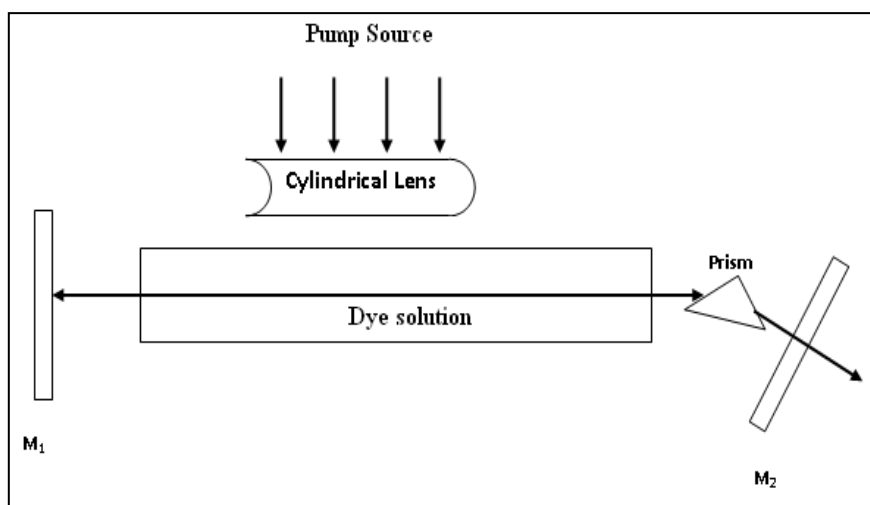
Fig 3.10 Transversely pumping system

3.14. Solvent Effects on Dye Emission Parameters

Solvent interactions with solute molecules are predominantly electrostatic and may be four types: (a) induced dipole-induced dipole, (b) dipole-induced dipole, (c) dipole-dipole or (d) hydrogen bonding types. The forces which stabilize the liquid state are the weak intermolecular forces such as electrostatic forces, hydrogen bonding and transfer interaction[99].

The shifts in absorption and emission spectra of the dye solutions are caused by dielectric interactions which are long range in nature and also by specific interactions which are of short range [99].

Chemists have classified solvents into three categories according to their polarity.

3.14.1. Aprotic

Commonly in the context used, aprotic refers to a hydrogen atom attached to an electronegative atom. For our purposes that electronegative atom is almost exclusively oxygen. In other words, polar aprotic solvents are compounds that can be represented by

the general formula ROH. The polarity of the polar aprotic solvents stems from the bond dipole of the O-H bond. The large difference in electronegativities of the oxygen and the hydrogen atom, combined with the small size of the hydrogen atom, warrant separating molecules that contain an OH group from those polar compounds that do not. Examples of polar aprotic solvents are water (HOH), methanol (CH**3**OH), and acetic acid (CH**3**CO**2**H) [99].

3.14.2 Dipolar aprotic

Here the key word is aprotic. In the context used here, aprotic describes a molecule that does not contain an O-H bond. Solvents in this class all contain a bond that has a large bond dipole. Typically this bond is a multiple bond between carbon and either oxygen or nitrogen. Most dipolar aprotic solvents contain a C-O double bond. Examples are acetone [(CH$_3$)$_2$C=O] and ethyl acetate (CH$_3$CO$_2$CH$_2$CH$_3$) [99].

3.14.3 Non-polar aprotic

Non-polar solvents are compounds that have low dielectric constants and are not miscible with water. Examples include benzene (C_6H_6), carbon tetrachloride (CCl_4), and diethyl ether $(CH_3CH_2OCH_2CH_3)$ [99].

Consider the absorption of light by a polar molecule capable of hydrogen, in a solvent of high polarity (dielectric constant) and having both hydrogen bond donor and acceptor properties (e.g. water). In the ground state the molecule will have a solvent cage in which the positive ends of solvent dipoles will be oriented about the negative ends of the solute dipole. Positively polarized hydrogen atoms of the solvent may be oriented toward lone pairs on the solvent (**Fig 3.11**) [76].
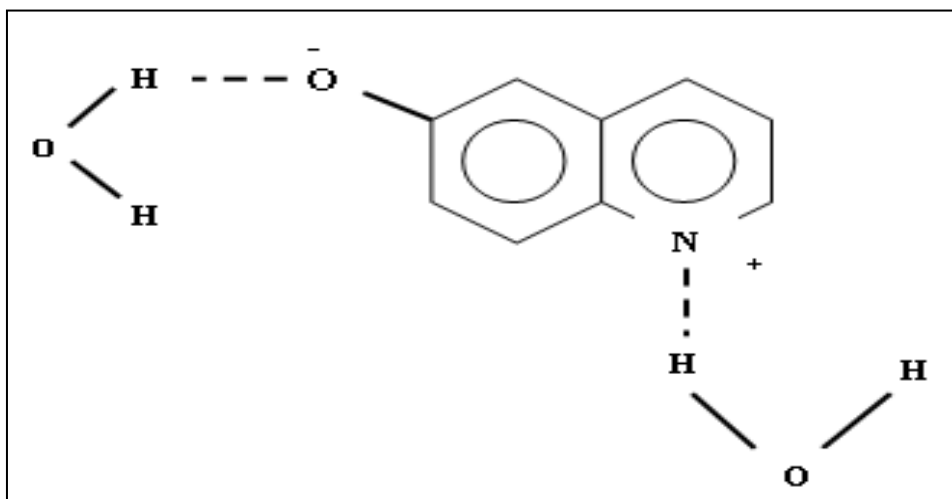
Fig 3.11 possible models of hydrogen bonding and solvent dipole orientation in various Species derived from 6- hydroxyquinoline in water

The light absorption process alters the electronic distribution of the solute so that the electronic dipole moment of excited molecule is different from that of the ground state molecule. However, the absorption process is so rapid that it terminates with the excited molecule still in the ground state equilibrium solvent cage (i.e. in a Franck-Condon excited state)[76].

If the solute molecule becomes more polar in the excited, there will be greater electrostatic stabilization of the excited state, relative to the ground state, by interaction with the polar solvent (**Fig 3.12**). The greater the polarity of the solvent, the lower will be the energy of the Franck-Condon excited state. This type of behavior is characteristic of most from π to π^* and ICT transitions and is observed as a shift to longer wavelength of the absorption band width increasing solvent polarity[76].

In the event that the electronic dipole moment is lower in the Franck-Condon excited state than in the ground state, increasing solvent polarity will stabilize the

ground state to greater degree than the excited state and the absorption spectrum will
shift to shorter wavelength with increasing solvent polarity [76]
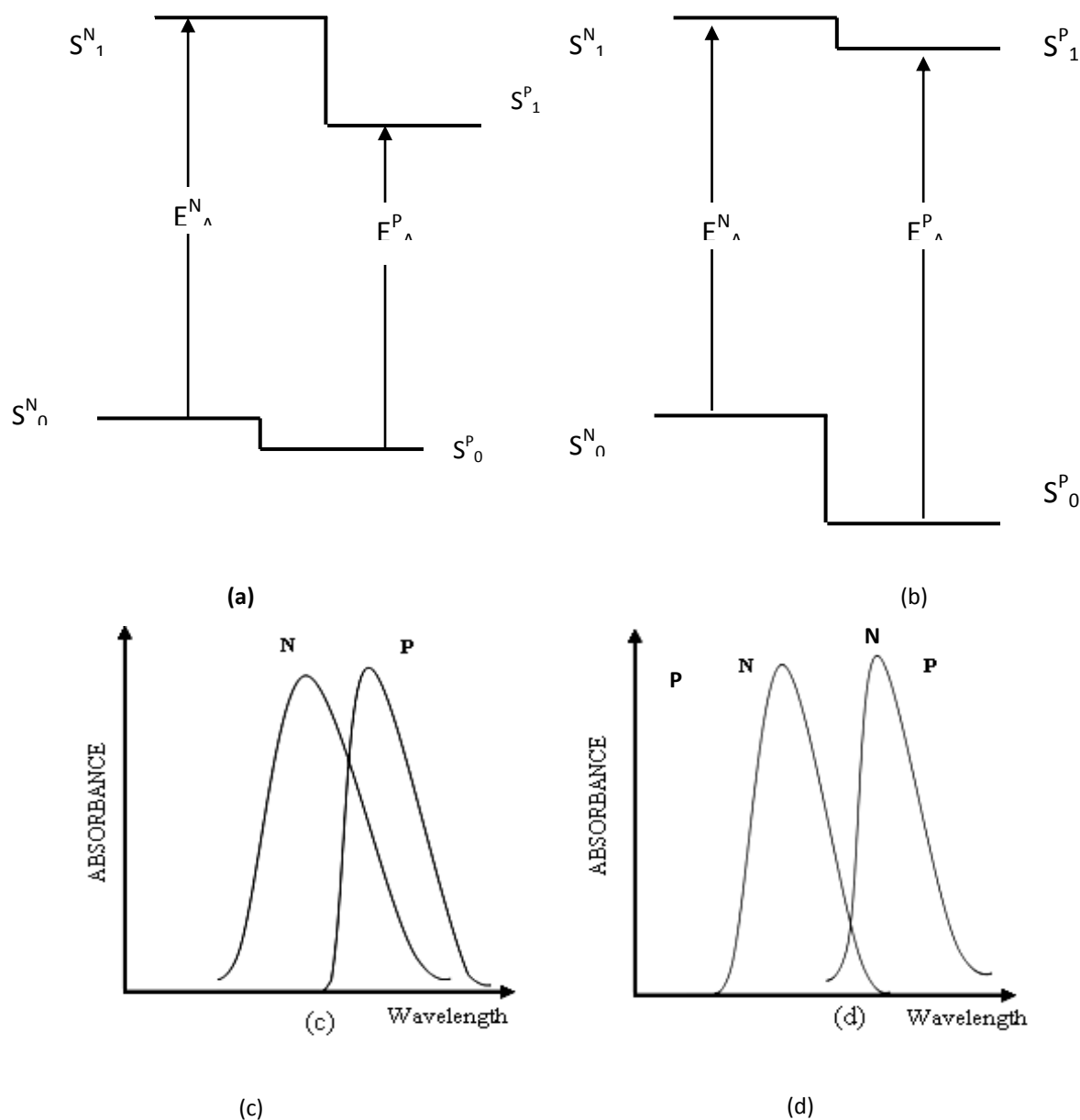
Fig 3.12 the effect of going from a non-polar solvent (denoted by N) to a polar solvent (denotedby P), upon the energy (E_A) of an absorptive transition (a) when the excited singlet stateto which absorption occurs (S_1) is more polar than the ground state (S_0) , (b) when the Excited state singlet state to which absorption occurs is less polar than the ground state,(c) and (d) represent the way the spectral bands corresponding to the transition in (a) and(b), respectively might appear.

Absorptive transitions of the $n \rightarrow \pi^*$ type are usually more affected by hydrogen bond donor properties of the solvent than by solvent polarity per se. If a nonbonding pair on a solute molecule is bound by hydrogen atom of the solvent, the hydrogen bonding interaction stabilizes the ground state as well as the n, π^* state of the solute. However, because the ground state molecule has two electrons in the nonbonding orbital and the excited state has only one, the stabilization of the ground state is greatest. As a result, the energies of $n \rightarrow \pi^*$ absorptions increase (the spectra shift to higher frequencies or shorter wavelengths) with increasing solvent hydrogen bond donor capacity. In a similar manner, but to a lesser degree, the positive end of the dipole of a polar solvent is capable of producing the same effect upon $n \rightarrow \pi^*$ absorption spectra [76].

Hydrogen bonding solvents also produce a dramatic effect upon ICT absorption spectra. Hydrogen bond donor solvents interacting with lone pairs on functional groups which are charge-transfer acceptors in the excited state (e.g. the carbonyl group), enhance charge-transfer by introducing a partial positive charge acceptor group. This interaction stabilizes the charge –transfer excited state relative to the ground state so that the absorption spectra shift to longer wavelength [76].

Hydrogen bond acceptor solvents produce shifts to longer wavelength when solvating hydrogen atoms on functional groups which are charge-transfer donors in the excited state (e.g. -OH, -NH$_2$). This is effected by the partial withdrawal of the positively charged proton from the functional group. Finally salvation of hydrogen atoms on functional groups which are charge-transfer acceptors in the excited state inhibits charge transfer by leaving a residual negative charge on the functional group. Thus, the latter interaction results in shifting of absorption spectrum to shorter wavelength [76].

In fluorescence molecules, subsequent to excitation to the Franck-Condon excited state, the ground state solvent cage reoriented itself to conform to new electronic distribution of the excited molecule. This solvent relaxation process involves reorientation of solute dipoles about new center of positive and negative charge in the excited molecule, and possibly the strengthening, weakening, breaking and making of hydrogen bonds because nuclear motion are involved, solvent relaxation is approximately contemporaneous with vibrational relaxation, taking 10^{-14} - 10^{-12} sec, and is rapid by comparison with the lifetime of lowest excited singlet state (10^{-8}sec). Consequently, fluorescence originates from the excited solute molecule in a thermally equilibrated solvent cage configuration which is lower in energy than Franck-Condon excited state, and generally even somewhat lower than the vibration ally relaxed insolated or weakly solvated excited molecule [76].

When fluorescence occurs, it terminates in the ground electronic state of the solute molecule, but because of rapidity of electronic transition, the molecule is still in the excited state equilibrium solvent cage (higher in energy than the thermally relaxed ground state). Rapid solvent relaxation then occurs (10^{-14} - 10^{-12} sec), and the solute molecule ultimately returns to ground state equilibrium solvent cage. Because the solvent relaxed excited state is lower in energy than the Franck-Condon excited state, and the Franck-Condon ground state (**Fig3.13**), fluorescence often occurs at considerably longer wavelength than would be anticipated purely on basis of vibrational relaxation. It is for this reason than $o - o$ bonds of fluorescence and absorption often do not coincide[76].
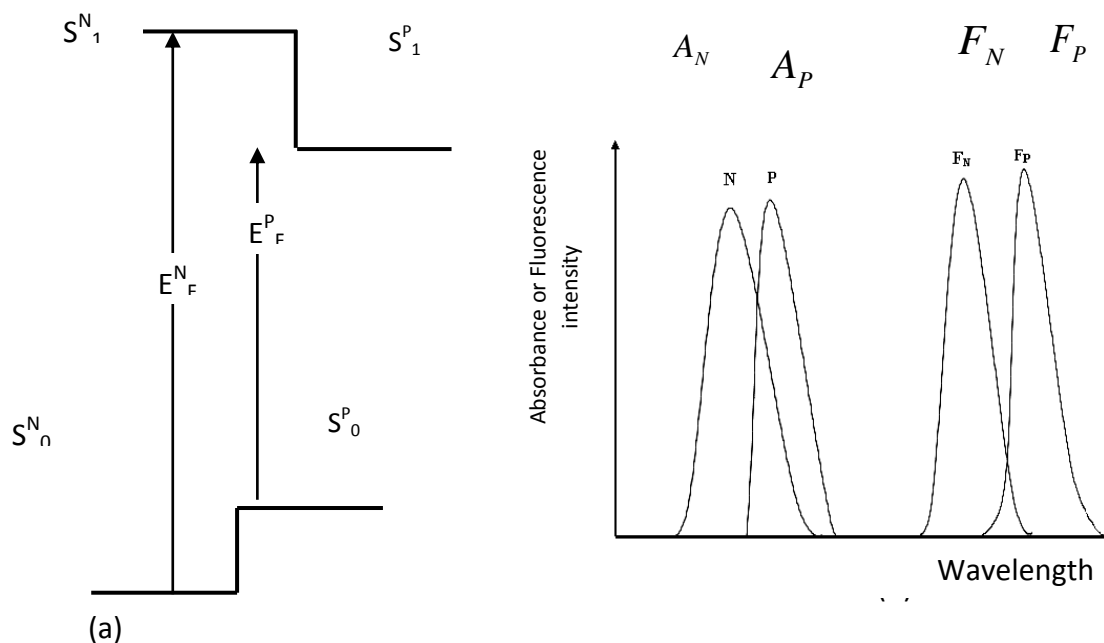
Fig 3.13 (a) The effect of solvent upon the energy of the fluorescence transition (E_F) of molecule which is more polar in the excited state (S_1) than in the ground state (S_0).Superscript N denotes non polar solvent; superscript P denotes polar solvent. **(b)**Representation of fluorescence band F_N and F_P which might be expected to correspond to the transition depicted in (a). The corresponding from S_0 to S_1 absorption bands (A_N and A_P) are also shown, illustrating the destruction of mirror image relationship between absorption and fluorescence in polar solvents.

Solvent polarity and hydrogen bonding effects upon fluorescence spectra are qualitatively similar to those upon absorptive spectra. For example, molecules which are more polar in the excited state usually show longer wavelength of fluorescence in more polar solvents. However, molecular sites of hydrogen bonding in the ground solvent cage may be altered in the excited state solvent cage. Since spectral shifts to longer or shorter wavelength resulting from dipolar or hydrogen bonding interaction may constructively or deconstructive additive, it is not unusual to find that in a given series

of solvents, the fluorescence shifts of a given solute may not parallel, even qualitatively, the absorption shifts in the same series of solvents [100].

The dependence of absorption and fluorescence spectra upon hydrogen bonding properties of the solvent are somewhat more involved than the dependence upon solvent polarity alone [101].

3.15. Concentration Effect

The argument developed, up to the present, for the spectral behavior of molecules is in very dilute solutions ($< 10^{-4} M$), where the interactions were predominantly of the solute solvent type. High concentrations of absorbing or luminescent species, in solution, may cause problems in the interpretations of molecular electronic spectra. Some of these problems arise from a practical point of view. However, some aspects of the spectroscopy of concentrated solutions arise from solute-solute interactions and their consideration is fundamental to the understanding of chemical spectroscopy [76].

It is well known that the limit of high absorber concentration, the linearity between absorbance and concentration, break down. Usually, this is observed as a diminution of the rate of increase of absorbance with increasing absorber concentration. In very concentrated solutions the absorbance may become infinite because all of exciting light will be absorbed before it can completely penetrate the sample cell [20].

However, at concentrations well below the limit of total absorption, the nonlinearity of absorbance with concentrations is due to chemical phenomenon in the ground electronic state. As the solute concentration is raised, the frequency of encounters between the solute molecules is increased. Often the solute molecules are capable of forming poly molecular aggregates or complexes in which the aromatic systems are coupled. When this phenomenon occurs, the complex species are formed at

the expense of the monomeric species whose absorption is being monitored, usually at fixed wavelength. If the aromatic systems of monomers are coupled in the aggregates, the complete absorption spectrum will usually reveal a shift to lower frequency resulting from the absorption by the polymeric species. However, even if the aromatic systems of the monomers comprising the aggregates are not coupled appreciably so that no red shift occurs, the effective concentration of absorbers is still diminished even though absorption still occurs principally at the original wavelength of measurement [76].

CHAPTER IV

Materials and Methods

4.1. Materials

4.1.1 Chemicals

All the chemicals materials are certified materials purchased from different companies shown in table (3.1). The chemicals were of analytical grade and were used without further purification as.

Table 4.1. List of the chemicals compounds, their manufacturers, grades and countries of production.

Reagent	Manufacturer	Grade	Country
Acetophenone	Scharlau	Extra Pure	Spain
4, dimethylaminobenzaldehyde	Sigma Aldrich	synthesis	Germany
4, cholorobenzaldehyde	ACROS	GR	Belgium
4, methylbenzaldehyde	ACROS	GR	Belgium
Hydrochloric Acid	LOBA Chemie	Analytical	India
Sodium Hydroxide	Chem Limited	GR	India
Methanol	Panreac	Absolute	Spain
Ethanol	Panreac	Absolute	Spain
Acetone	Panreac	Absolute	Spain
Dimethylformamide (DMF)	PRO	Absolute	Spain
Acetic acid	BDH	Absolute	England
Acetonitrile	BDH	Absolute	England
Tetrahydrofuran (THF)	CDH	Absolute	India
Chloroform	Sigma Aldrich	Absolute	Germany
Toluene	BDH	Analytical	England
Benzene	Panreac	Absolute	Spain

4.1.2. Glassware

Glass has a wide variety of functions which include volumetric measuring, holding or storing chemicals or samples, mixing or preparing solutions or other mixtures, containing lab processes like chemical reactions, heating, cooling, distillation, separations including chromatography, synthesis and spectroscopic measurement table (3.2) listed the glassware that were used.

Table 4.2.List of the glassware, their manufacturers, grades and countries of production.

Glassware	Manufacturer	Grade	Country
Beaker (100, 250, 500 ml)	Global labware	A	India
Measuring cylinders (10, 20, 100 ml)	Global labware	A	India
Volumetric flasks (100, 250 ml)	Global labware	A	India
Pasteur Pipettes	Global labware	A	India
Cuvette	Global labware	A	India
Glass dropper	Global labware	A	India
Condenser	Global labware	A	India
Round bottom flask (250ml)	Global labware	A	India
Buchner funnel (250ml)	Global labware	A	India
Glass funnel (250ml)	Global labware	A	India
Watch glass	Global labware	A	India
Pistol & mortar	Global labware	A	India

4.2 Synthesis of lasing chalcones

4.2.1. Synthesis of the (DMAPPP)

The 1-(phenyl)-3-(4- N, N dimethyl amino phenyl)-2-propen-1-one (DMAPPP) (**Fig 4.1a**) was synthesized using condensation reaction between acetophenone (0.01 mole) and 4-dimethylaminobenzaldehyde (0.01 mole) in basic condition of sodium hydroxide (1.0 gm), in ethanol (50ml). The vessel was left overnight under steering at room temperature and then the yield was recrystallized from ethanol. The crystal was washed with distilled water and it had been left to dry [102]. The synthetics compounds were characterized by FTIR, H^1NMR and UV-Vis spectroscopy.
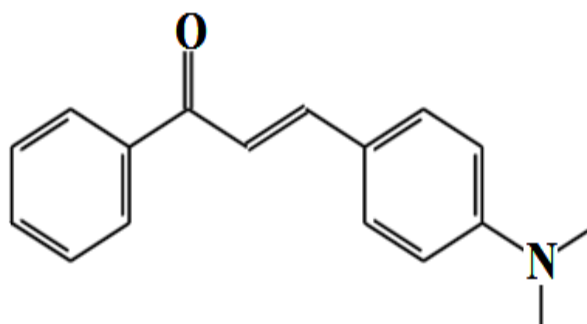
Fig (4.1a) Molecular Structures (DMAPPP).

4.2.2. Synthesis of the (MDMAPP)

A green synthesis of the 1-(4-methylphenyl)-3-(4- N, N dimethyl amino phenyl)-2-propen-1-one (MDMAPP) (**Fig 4.1c**) was performed using a condensation reaction of 4-dimethylaminobenzaldahyde (0.01 mole) and 4-methylacetophenpne (0.01 mole) in basic condition of Sodium Hydroxide (1.0 gm.) and ethanol (50 ml) as a solvent. The product was recrystallized from ethanol and water, filtered, washed with water and left to dry[102].The synthetics compounds were characterized by FTIR, H^1NMR and UV-Vis spectroscopy.
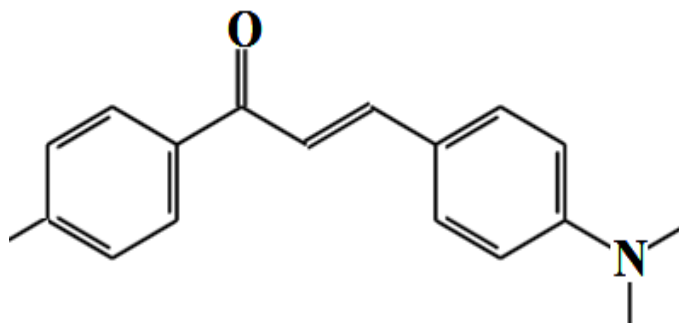
Fig (4.1b) Molecular Structures of (MDMAPP).

4.2.3. Synthesis of the (CPDAPP)

The 1-(4-chloridephenyl)-3-(4- N, N dimethyl amino phenyl)-2-propen-1-one (CPDAPP) (**Fig4.1c**) was fabricated via simple reaction between 4-dimethyl aminobenzaldahyde (0.01 mole) and 4-chloroacetophenpne (0.01 mole) in the presence of   NaoH (1.0 gm.) and   alcohol (CH$_3$CH$_2$OH 50ml). The mixture was placed in the glass vessel and left for steering at room temperature overnight, afterward the product recrystallized from ethanol and washed with distilled water in order to achieve pure final product[103]. The CPDAPP was characterized by FTIR, H^{1}NMR and UV-Vis spectroscope
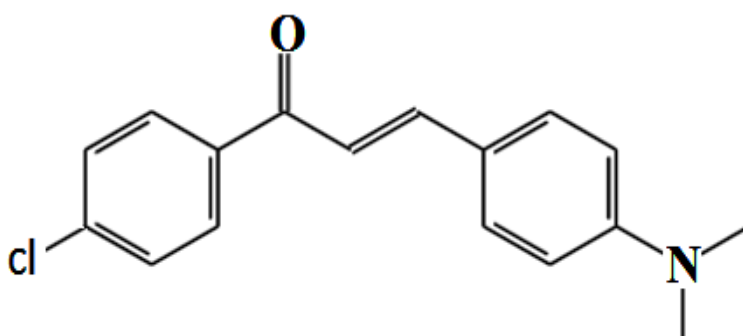
Fig (4.1c) Molecular Structures (CPDMP).

4.3 Materials characterizations

In this project three chalcones dyes; DMAPPP, MDMAPP and CPDAPP were synthesized and dissolved in a wide range of organic solvents, which are mentioned above. The molecular weights (MW) were calculated according to their molecular structures as given in **Fig.4.1** (a), (d) and (c) respectively. The solvents used were (spectroscopic grade) benzene, Toluene, ethanol, Methanol, acetone, Dimethylformamide (DMF), Acetonitrile, Chloroform, Acetic acid, and Tetrahydrofuran (THF). The purity for each solvent was (99.8%).The molarity (M) calculation was done using the following chemical formula.

$$M = \frac{n \times V}{100} \tag{4.1}$$

$$n = \frac{weight}{molar\ mass} \tag{4.2}$$

Where n number of moles and v the volume

A set of solutions was prepared by dissolving synthesized chalcones in different solvents with different concentrations. The UV-VIS absorption spectra for the specimens were obtained in the range of 200 to 800 nm by using Perkin Elmer spectrophotometer. The fluorescence spectra were recorded using a Perkin Elmer LS45 spectrofluorometer. For the ASE experiments, a chalcones was dissolved in organic solvents, the solutions were placed in a quartz cuvette its dimensions was (10mm ×10mm× 40mm). The Nd: YAG laser of 355 nm was used as an excitation source with pulse duration and repetition rate of 6 ns and 1~10 Hz, respectively. A quartz cylindrical lens with a focal length of 5 cm was used to focus the pump beam on the cuvette which was tilted to avoid the feedback . The ASE spectrum was collected from the sides of the

cuvette by a small slit of the spectrograph, which was connected to a CCD camera (Andor).

4.3.1. Absorption Instrumentation

Perkin Elmer lambda 40 UV-VIS Spectrophotometer was used for optical studies. The excitation source is a special Xenon flash tube that produces continuous radiation over the spectral range. The path of the radiation is shown in (**Fig 4.2**). Light from the source is focused by the ellipsoidal mirror (M (E)) and reflected onto the gating, and the beam passes through the slit. By the combination of grating and slit, the wavelength could be chosen; the specified wavelength passes to the beam splitter (BS), where the beam light divided into two parts, one part passes to the reference, and the other passes to the sample [104].

The beam of light passing through the reference and falling on the photomultiplier tubes (PMT) is recorded as I_0. When the instrument records I_0, the beam from the sample is kept blocked. After the measuring I_0, the chopper will allow the light from the sample and measured as I.

The optical density (A) defined as[82]:

$$A = \log\left(\frac{I_0}{I}\right) \qquad (4.3)$$

Where:

A is optical density. I_0 is reference intensity and I is sample Intensity.

The grating rotated for a wide range of wavelengths λ. When A, the optical density, plotted against the wavelength λ the absorption spectra are obtained. While A is a function of concentration, molar excitation coefficient of the solution (4.3).

$$A(\lambda) = \log\left(\frac{I_0}{I(\lambda)}\right) = \varepsilon(\lambda)c\,\ell \qquad (4.4)$$

Where:

ε (λ) is molar extinction coefficient of the solution .

c is concentration of the solution.

ℓ is the path length of the sample.
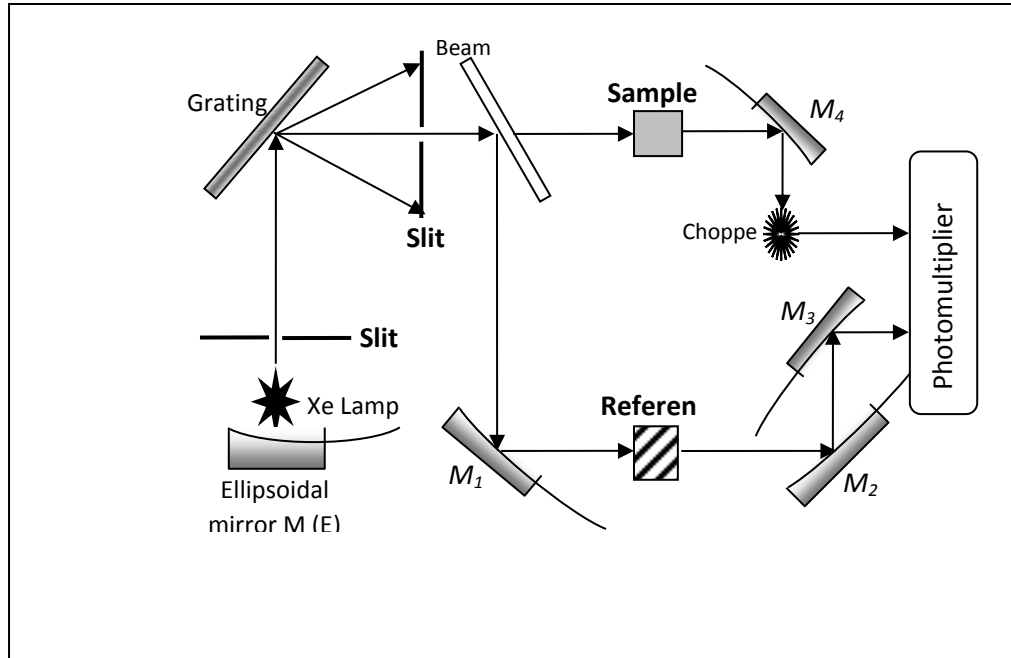
Fig 4.2 Schematic of Perkin Elmer lambda 40 UV-VIS Spectrophotometer LAMDA 40.
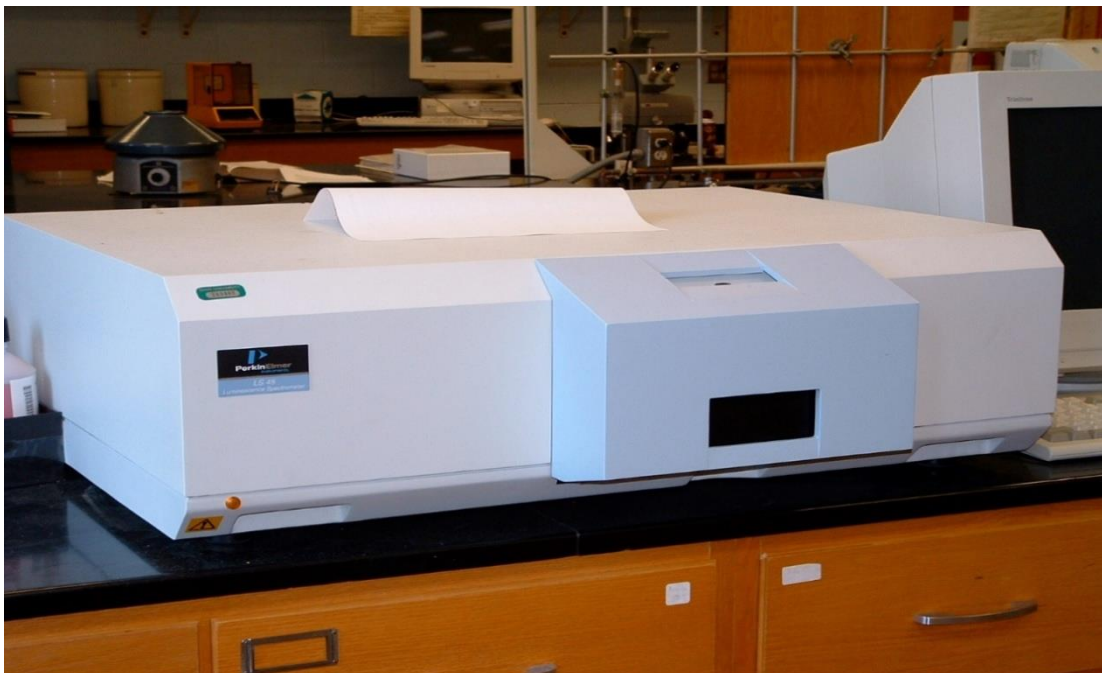
Fig4.3 Perkin Elmer lambda 40 UV-VIS Spectrophotometer LAMDA 40 .

4.3.2. Fluorescence Instrumentation

      Perkin Elmer LS45 luminescence was used to get spectra of fluorescence. The apparatus were operated at temperature from 20ºC. The excitation source is a special Xenon flash tube that produces an intense short duration pulse of radiation over the spectral range.(**Fig.4.3**) showed the path of the radiation in the instrumentation [106].

      Energy from the source focused by the ellipsoidal mirror M (E) 5 and reflected by the toroidal mirror onto entrance slit of the excitation monochromator. The monochromator consists of the entrance slit, a gating, a spherical mirror and exit silt. A narrow wavelength band emerges from the exit slit, with the center wavelength being determined by the setting of the grating, the angle of which controlled by a stepper motor. The majority of the excitation beam transmitted to the sample area via the focusing toroidal mirror M (T) 1, a small proportion reflected by the beam splitter onto the reference photodiode. To correct for the response of the reference photodiode a rhodamine correction curve is stored within the instrument. Rhodamine dye absorbs energy from 320 to 520 nm and fluorescence about 650 nm with nearly constant quantum efficiency[106].

      Energy emitted by the sample is focused by the toroidal mirror M (T)1 into the entrance slit of the emission monochromator. The monochromator consist of entrance slit, a spherical mirror M(S)3, a grating and the slit. A narrow wavelength band emerges from the exit slit, with the center wavelength being determined by the setting of the grating, the angle of which controlled by stepper motor. The excitation and emission monochromators can be scanned over their range independently[106].

      The spectral ranges of the monochromators are:

(1) Excitation monochromator 200 nm to 800 nm and zero order.

(2) Emission monochromator 200 nm to 900 nm and zero order.
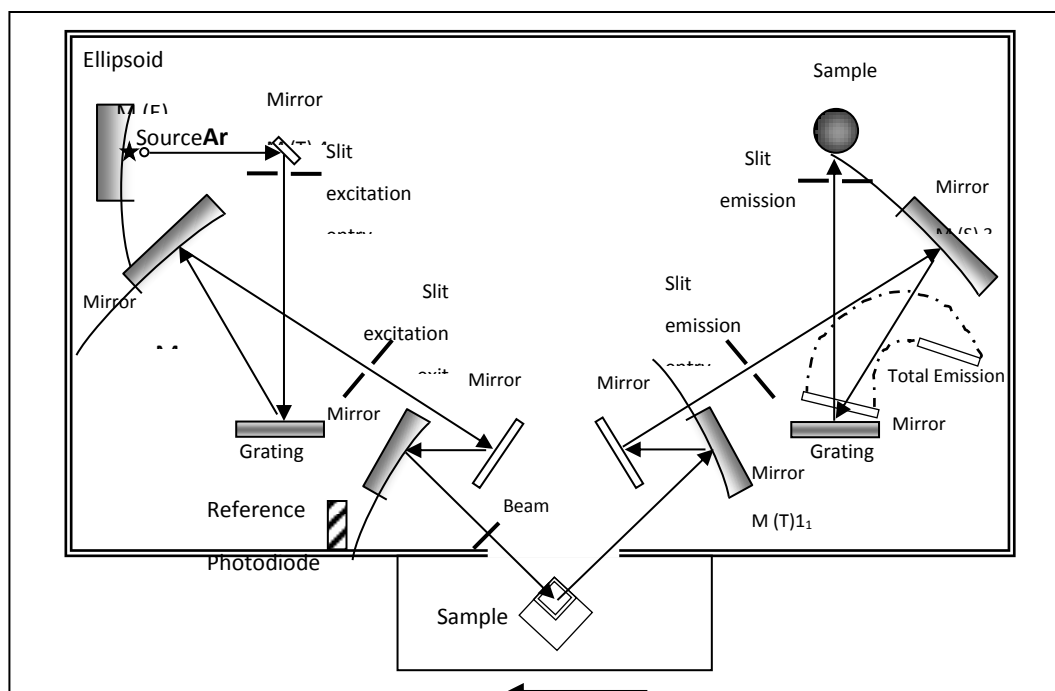
Fig 4.4 The scheme of Perkin Elmer LS45 luminescence.

Fig 4.5 Perkin Elmer LS45 luminescence.

4.3.3 Nd: YAG Laser

To study the excited state behavior of polymer dyes Nd: YAG laser was used as high power pulsed laser at 355 or 532nm (absorption maximum for polymer dyes). Nd: YAG obtained from Continuum Solar Co. It consists of a laser head, this modular design incorporating a rod, a flash lamp and coupling medium. It has a linear flash lamp which is in a close coupled configuration surrounded by a high brilliance magnesium oxide diffuser [107].

This results in a high pumping efficiency that minimizes thermal loading and reduces power consumption. These features combine to create the excellent pumping homogeneity required for producing high gain, superior quality beams [107].

The head is designed to pump Nd^{+3} doped YAG. The doping levels vary from 0.9 to 1.4%. The YAG rod ends have hard dielectric anti-reflective coatings (AR). The rod length is 115mm measured along the optical axis, and the diameter of the rod is 6mm [107].

The head is pumped by a linear flash lamp. The lamp has a voltage polarity that must be observed. The discharge system of the flash uses a negative, critically damped pulse (-1.8 KV) with a duration of 200 microseconds full width half max (FWHM). The gas in the flash lamp is xenon with a pressure of 1-3 atmospheres. Flash lamp and laser rods must be cooled by distilled, deionized water [107].

The Solar series can generate laser at the Nd: YAG fundamental wavelength (1064nm) or its second harmonic (532nm), third harmonic (355nm) or fourth harmonic (266nm). This is achieved by passing the fundamental beam through specific crystals called second harmonic generation (SHG), or in third harmonic generation (THG), or fourth harmonic generation (FHG) second. These optical harmonic generators are

positioned at the end of the bench, and can be optimized with adjustment knobs located on the top and in the right [107].

In this project the second and the third harmonic of Nd: YAG laser ($\lambda = 532$ nm & 355nm) were used as excitation source as shown in (**Fig 4.4**), with these operational parameters[107]:

Pulse width = 11ns.

Beam divergence at full width at half maximum (FWHM) = 1m radian

Spot size = 1mm.

Pulse energy variable from 1 to 280mJ.

Energy stability = 3.5%.
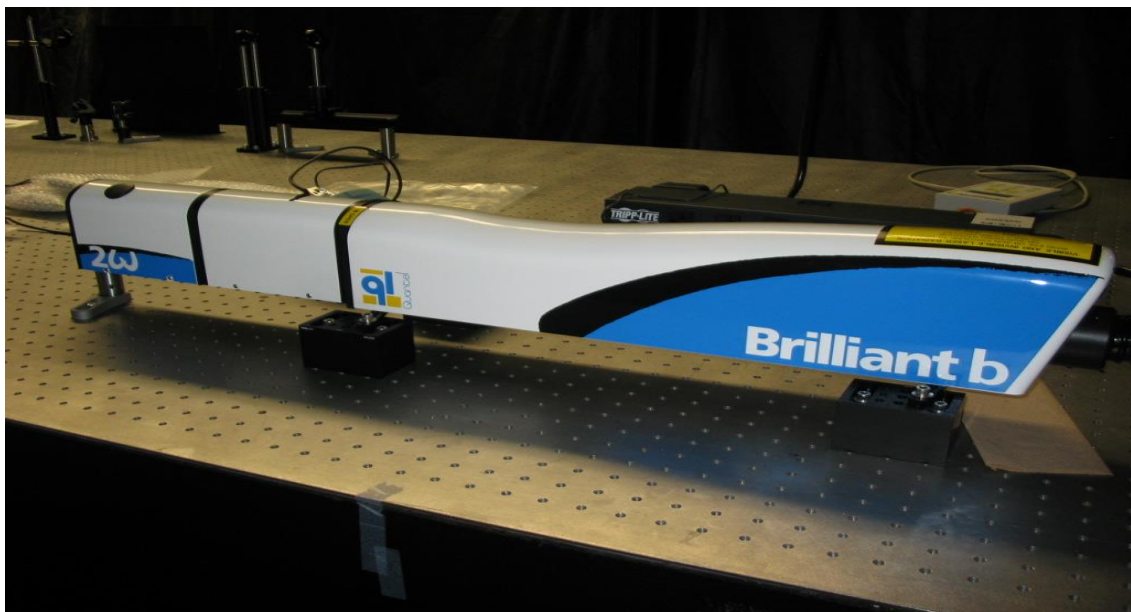
Fig 4.6 Nd: YAG Laser.

4.3.4 Charge-Coupled Device (CCD)

A charge-coupled device (CCD) is a sensor for recording images, consisting of an integrated circuit containing an array of linked or coupled, capacitors. Under the control of an external circuit, each capacitor can transfer its electric charge to one or other of its neighbors. CCDs are used in digital photography and astronomy (particularly in photometry, optical and UV spectroscopy). Solar M226 laser CCD was used for optical analysis as shown in (**Fig 4.5**) [108]
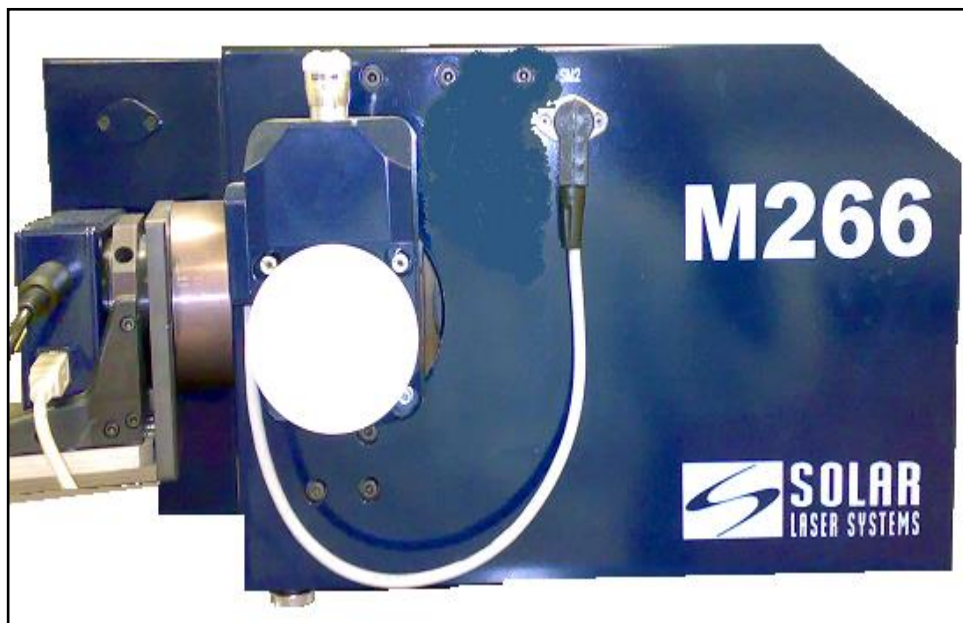
Fig 4.7 Charge-Coupled Device (CCD).

4.3.5 ASE Measurement and Instrumentation:

The laser beams (355 and 532nm) of Nd: YAG were focused onto a thin line image by a quartz cylindrical lens of focal length 5cm to perform transverse excitation of the dye solution taken in a quartz cuvette (1cm ×1cm × 4cm) and kept at an angle of 200 to avoid Fresnel feedback as shown in (**Fig 4.6**). When conditions like the pump power and concentration were optimum, this excitation produces single- pass optical gain and consequently amplified spontaneous emission (ASE) in the dye solution in the direction perpendicular to the pump laser beam propagation (transversely excited dye

laser TEDL). The ASE always emitted as a cone of light with an approximately elliptical cross section. This was collected by CCD camera to record ASE spectra.
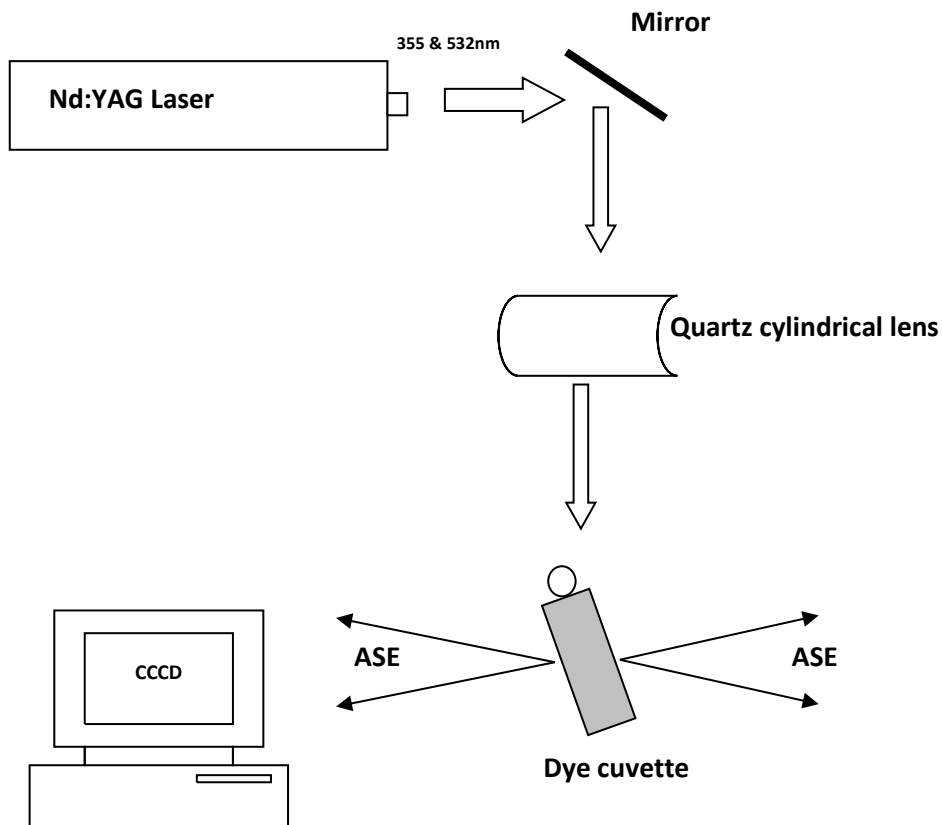
Fig 4.6 Experimental arrangement for transverse excitation of dye solution.

CHAPTER V

5. Results and Discussions

5.1. Introduction

This chapter is divided into two parts, the first part explains the photophysical properties such as absorption, fluorescence, stokes' shift, quantum yield of fluorescence and amplified spontaneous emission (ASE) spectra a new laser medium of 3-(4-(dimethylamino) phenyl)-1-phenyl-(2E)-propen-1-one (DMAPPP) in different organic solvents under a wide range of concentrations.

The second part contents the photophysical properties of DMAPPP were compared with two laser dyes which are; 1-(4-chloridephenyl)-3-(4- N, N dimethyl amino phenyl)-2-propen-1-one (CPDAPP) and 1-(4-methylphenyl)-3-(4- N, N-dimethyl amino phenyl)-2-propen-1-one (MDMAPP) that have closely related chemical structure.

5.2. PART (I)

5.2.1. Spectral Properties of DMAPPP

2.2.1.1. Absorption

The absorption spectra of 3-(4-(dimethylamino)phenyl)-1-phenyl-(2E)-propen-1-one (DMAPPP) in acetone were recorded for a wide range of concentrations from 0.65mM to 6.5mM. It was found that there was one absorption peak at 405 nm; the shape of the absorption spectra remained the same irrespective of the concentration, although the optical density increased with an increasing of concentration as shown in (**Fig 5.1**) This is an indication of the absence of *dimer* over all concentrations used.
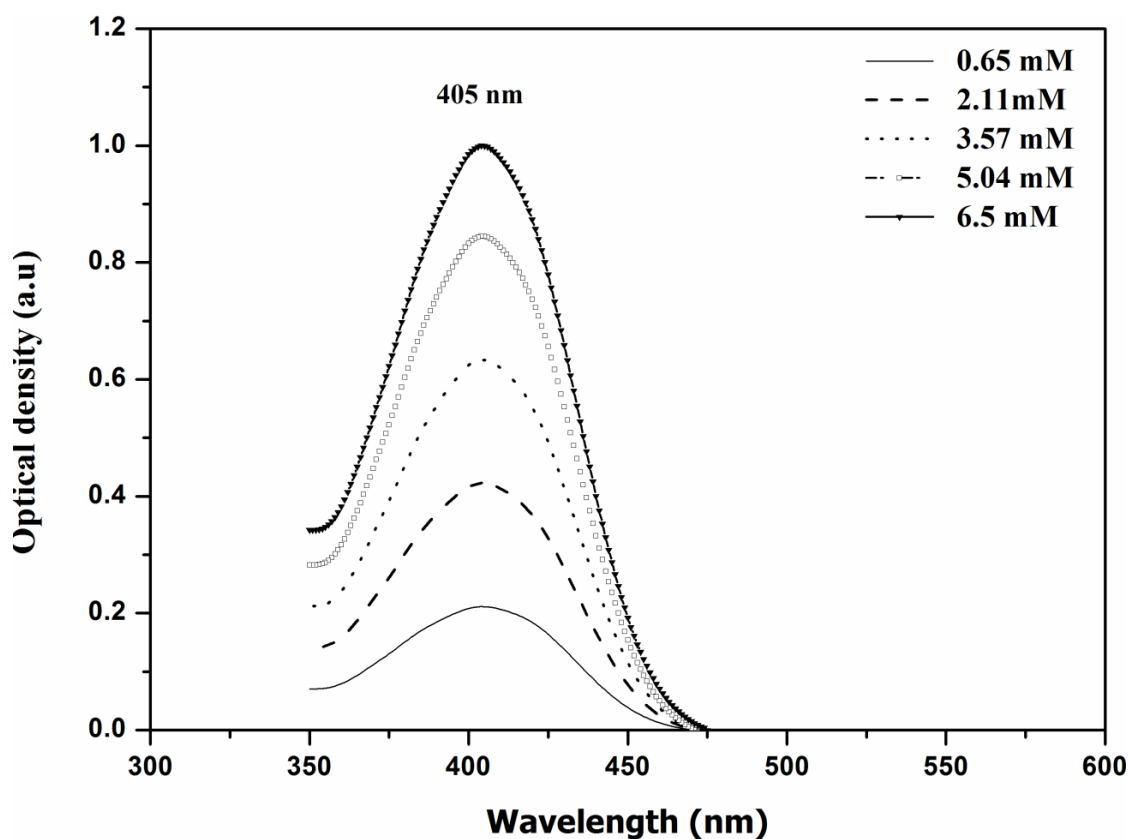
Fig 5.1.Absorption spectra of DMAPPP in acetone for different concentrations from 0.65-6.5 mM

2.2.1.2. Fluorescence

The fluorescence spectra of DMAPPP in acetone were recorded for above range of concentrations (0.65mM -6.5mM). The fluorescence spectra showed one band at 525 nm, see (**Fig.5.2**). The fluorescence spectral profile did not change irrespective of concentration for this dye. Moreover, the intensity decreased with an increasing the concentration. This indicates that the absence of excimer or exciplex for these dye solutions over all studied concentrations, as shown in (**Fig.5.2**).
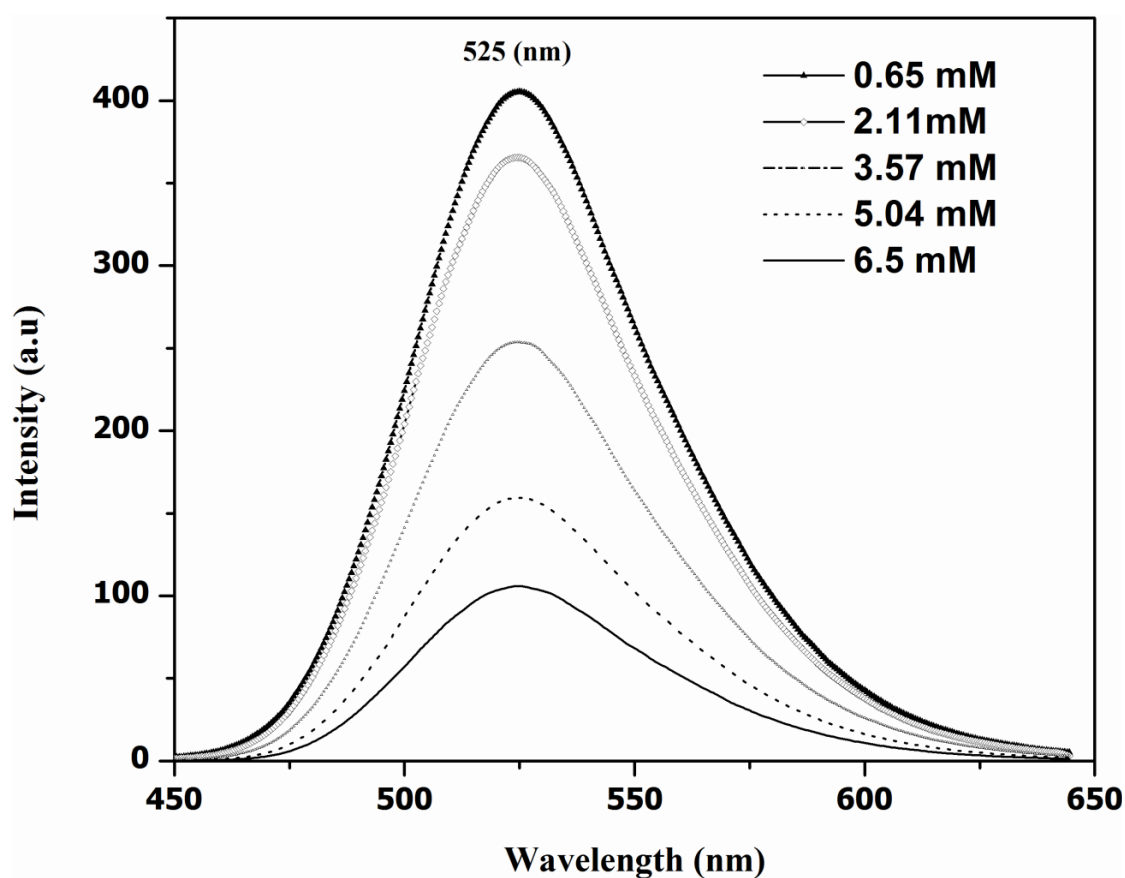
Fig 5.2 Fluorescence spectra of DMAPPP in acetone for different concentrations from 0.65-6.5 mM .

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5.2.1.3. Dependence of absorption and fluorescence of DMAPPP on the solvent

Having discussed the effect of the concentrations on the spectral properties of DMAPPP, here the influence of the solvents on the absorption and fluorescence spectra will be discussed. DMAPPP was dissolved in different organic solvents with different dielectric constant. The concentration of these solutions was fixed to be 0.65mM. DMAPPP exhibits a large red shift in both absorption and emission spectra as solvent polarity increased. It could be seen that the dielectric constant of the solvents plays an important role for the absorption and emission bands, as showing in (**Fig 5.3a&b**) and (**table.5.1**).
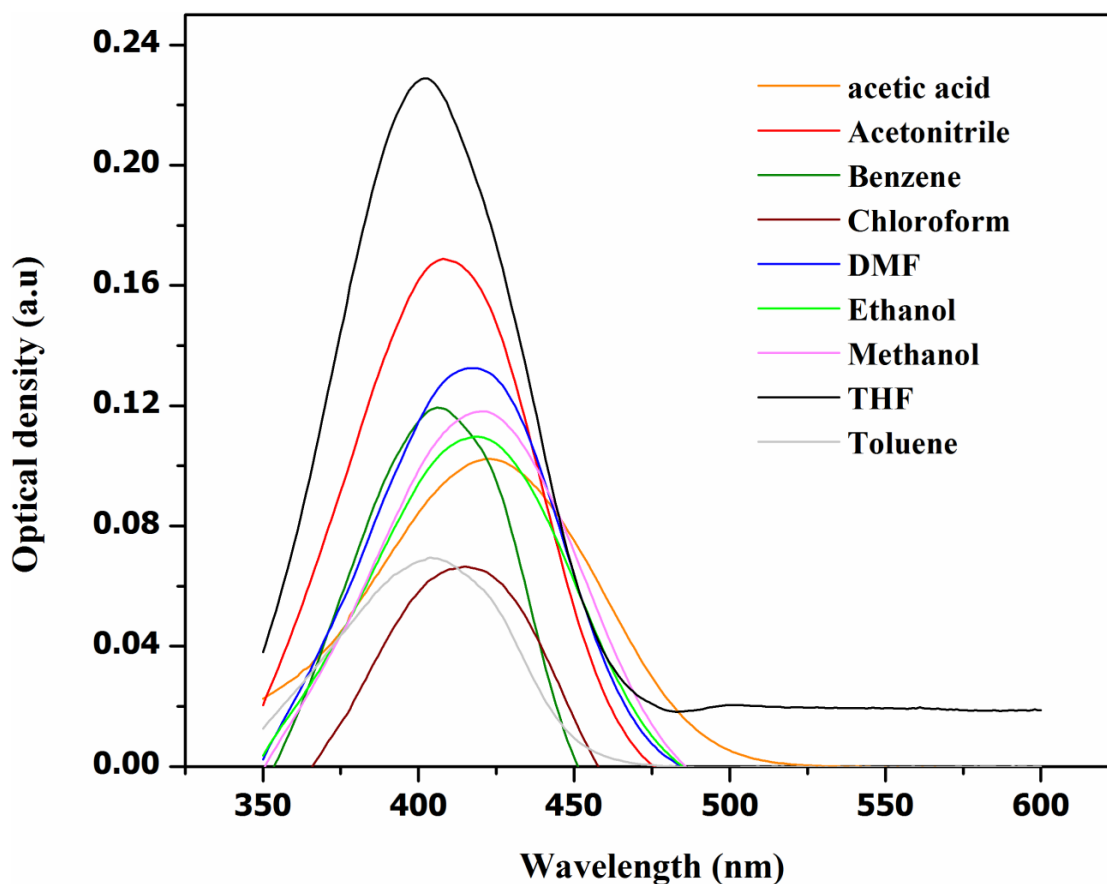
Fig 5.3a Absorption spectra of DMAPPP in different concentrations Solvent.
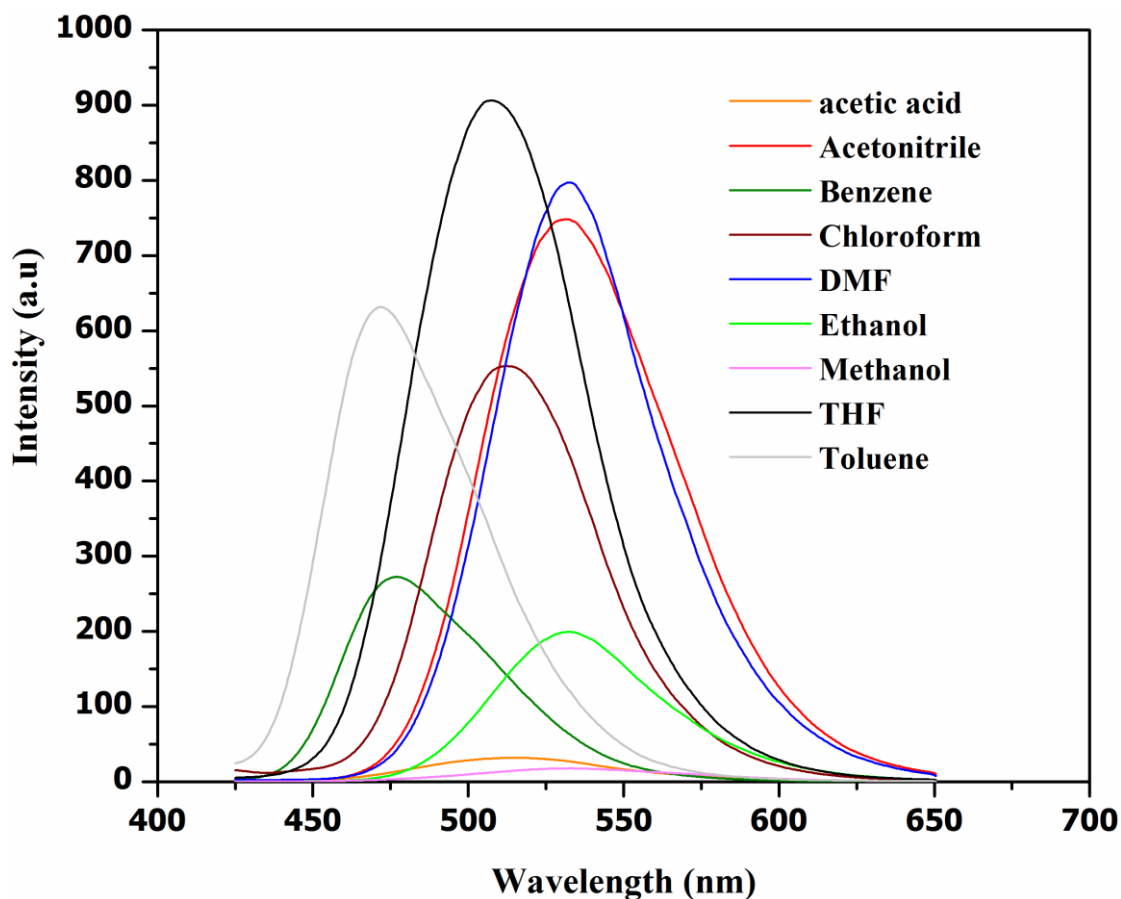
Fig 5.3b Fluorescence spectra of DMAPPP in different concentrations Solvent

Table.5.1: The spectral properties of DMAPPP in different solvents.

Solvent	Dielectric constant (ε)	λ_{max}	
		Absorption	Fluorescence
Benzene	2.27	407	477
Toluene	2.38	406	470
Chloroform	4.81	417	510
Acetic acid	6.15	423	517
Tetrahydrofuran (THF)	7.58	404	506
Acetone	20.7	407	525
Ethanol	24.5	420	530
Methanol	32.7	421	531
Dimethylformamide (DMF)	36.7	419	531
Acetonitrile	37.5	410	532

5.2.1.4. Stokes' shift

DMAPPP was dissolved in various organic solvents with different dielectric constants. The concentration of these solutions was fixed at0.65mM. The changes in the absorption and fluorescence spectra were observed (the fluorescence spectra were recorded at the excitation wavelength of 400 nm). (**Fig.5.4)** shows the variation of the Stokes' shift as a function of the dipole factor of the solvent, as defined by Metaga and Tsuno [87-89]. It can be seen that DMAPPP in the solution undergoes significant changes in the electron delocalization and becomes highly polar in the excited state than in the ground state. The Stokes' shift has a linear variation with the dipole factor, using equation (3.20).

(**Fig5.4)** shows a plot of the Stokes' shift as a function of dipole factor for representative solvents. This dipole factor is a measure of dipole-dipole interaction between the solvents and the solute. This result indicates this dye exhibits large changes in the dipole moment in the excited state.

Table.5.2: Stokes' shift of DMAPPP

Solvent	Dielectric constant (ε)	refractive index (n)	Dipole factor	DMAPPP λ max		DMAPPP ν		
				λ Absorption	λ Fluorescence	ν Absorption (nm-1)	ν Fluorescence (nm-1)	ν Absorption − Fluorescence (cm-1)
Benzene	2.27	1.5011	0.001642	406	477	0.002457	0.002096	3605.664
Toluene	2.38	1.4969	0.013235	404	471.5	0.002463	0.002128	3353.946
Chloroform	4.81	1.4458	0.148295	415	512	0.002398	0.001959	4392.177
Acetic acid	6.15	1.3716	0.202174	422	512	0.002364	0.001934	4298.302
(THF)	7.58	1.4072	0.209572	402	507.5	0.002475	0.001974	5009.139
Acetone	20.7	1.3587	0.284307	405	525	0.002457	0.001905	5522.406
Ethanol	24.5	1.3614	0.288687	418	532	0.002381	0.001883	4977.132
Methanol	32.7	1.3284	0.308587	421	533	0.002375	0.001874	5008.827
(DMF)	36.7	1.4305	0.27438	418	532.5	0.002387	0.001878	5087.006
Acetonitrile	37.5	1.3441	0.305416	408	531.5	0.002439	0.001894	5450.85
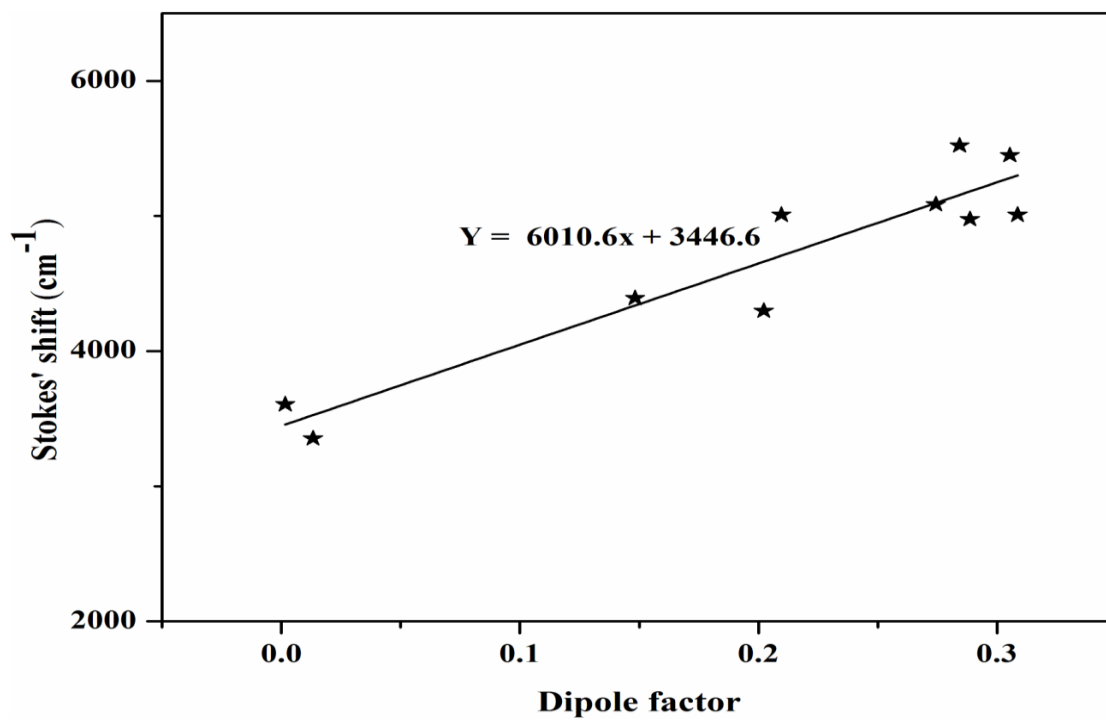
Fig 5.4 Variation in the Stokes' shift of DMAPPP in solution with a dipole factor for different solvents.

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5.2.1.5. Quantum yield of fluorescence

The fluorescence quantum yield (Φ_F) of DMAPPP was measured using diluted solutions. The concentration was kept at 0.65mM for each solution. Rhodamine 6G (Rh 6G) in methanol has a known fluorescence quantum yield (Φ_F) of 0.94. A 0.65mM of Rh 6G in methanol was taken as the standard for measurements. The quantum yield can be measured are substituted in equation (5.3) [109]

$$\Phi_F(s) = \Phi_F(R)\left[\frac{\int I_S(\overline{v})dv}{\int I_R(\overline{v})dv} \times \frac{A_R}{A_S} \times \frac{n_S^2}{n_R^2}\right] \qquad (5.1)$$

Where the indices **S** and **R** refer to the sample and reference, respectively, and the integral over **I** represent the area under the fluorescence spectrum. **A** is the optical density, and **n** is the refractive index of the solvents.

The solvents' influence upon the spectral properties is the Stokes shift, which is a measure of changes in the dipole movement of the species when it goes from the ground state to an excited state.

Table.5.3 shows the quantum yields of fluorescence (Φ_F) for DMAPPP.

Solvent	Dielectric constant (ε)	ϕ_F DMAPPP
Benzene	2.27	0.27
Toluene	2.38	0.24
Chloroform	4.81	0.66
Acetic acid	6.15	0.05
THF	7.58	0.96
Acetone	20.7	0.88
Ethanol	24.5	0.37
Methanol	32.7	0.02
DMF	36.7	0.93
Acetonitrile	37.5	0.66

5.2.2.1. Amplified spontaneous emission (ASE) of DMAPPP

To study the ASE properties of DMAPPP under high power excitation, DMAPPP was dissolved in acetone, with the concentration fixed at 1mM. This solution was transversely excited with a UV laser at 355 nm. At a pump power of 3 mJ, the ASE spectrum was recorded. Note that this was the minimum concentration and the minimum pump power excitation for DMAPPP to produce an ASE spectrum. **(Fig.5.5)** shows ASE peak at 530 nm with a narrow spectral bandwidth (full width at half maximum (FWHM)) 6 nm. This peak is coinciding with the maximum of the fluorescence emission spectrum at this concentration.
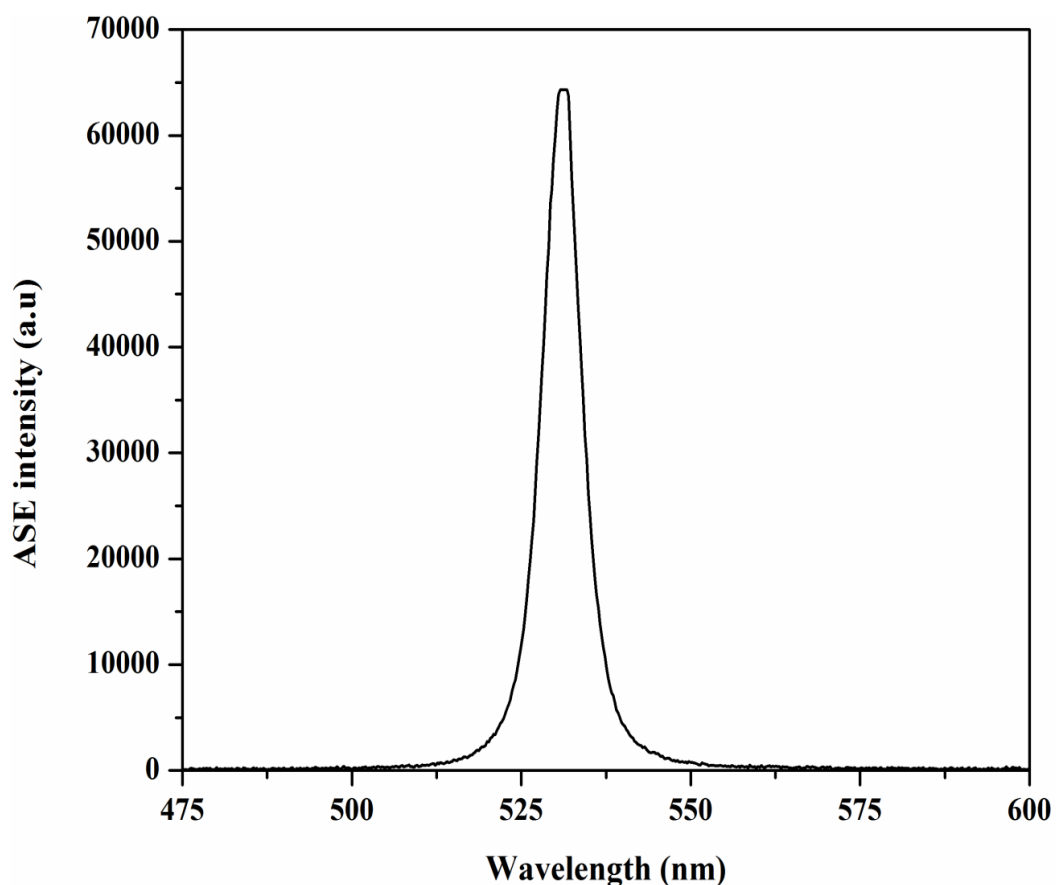
Fig 5.5 ASE spectra of DMAPPP in acetone at a concentration of 1mM

5.2.2.2. Dependence of ASE on Solvent type

Table.5.3 shows the ASE spectra of DMAPPP dissolved in different solvents having different polarities under identical conditions; the concentration was kept at 6.5mM for each solutions. The pump power was fixed at 9mJ. In general, it was found that when the dielectric constant increases the emission wavelength increasingly red shifted. In addition, The ASE in acetic acid, methanol, benzene and toluene was not detected even at high pump power energy and concentration. In toluene and benzene this may be due to the lowest solubility of the DMAPPP for these solvents. The absence of the ASE spectra in acetic acid may be due to the protonation of N-dimethylamino group of DMAPPP with responsible for their photo properties. Here the methanol could play similar role by deactivation of the lone pair of N-dimethylamino group by hydrogen bonding; this slightly appears in ethanol which gives poor ASE.

Table.5.4: The spectral and ASE properties of DMAPPP in different solvents

Solvent	Dielectric constant (ε)	λ_{max} DMAPPP		
		Absorption	Fluorescence	ASE
Benzene	2.27	407	477	----
Toluene	2.38	406	470	----
Chloroform	4.81	417	510	523
Acetic acid	6.15	423	517	----
THF	7.58	404	506	515
Acetone	20.7	407	525	532
Ethanol	24.5	420	530	548
Methanol	32.7	421	531	----
DMF	36.7	419	531	548
Acetonitrile	37.5	410	532	547
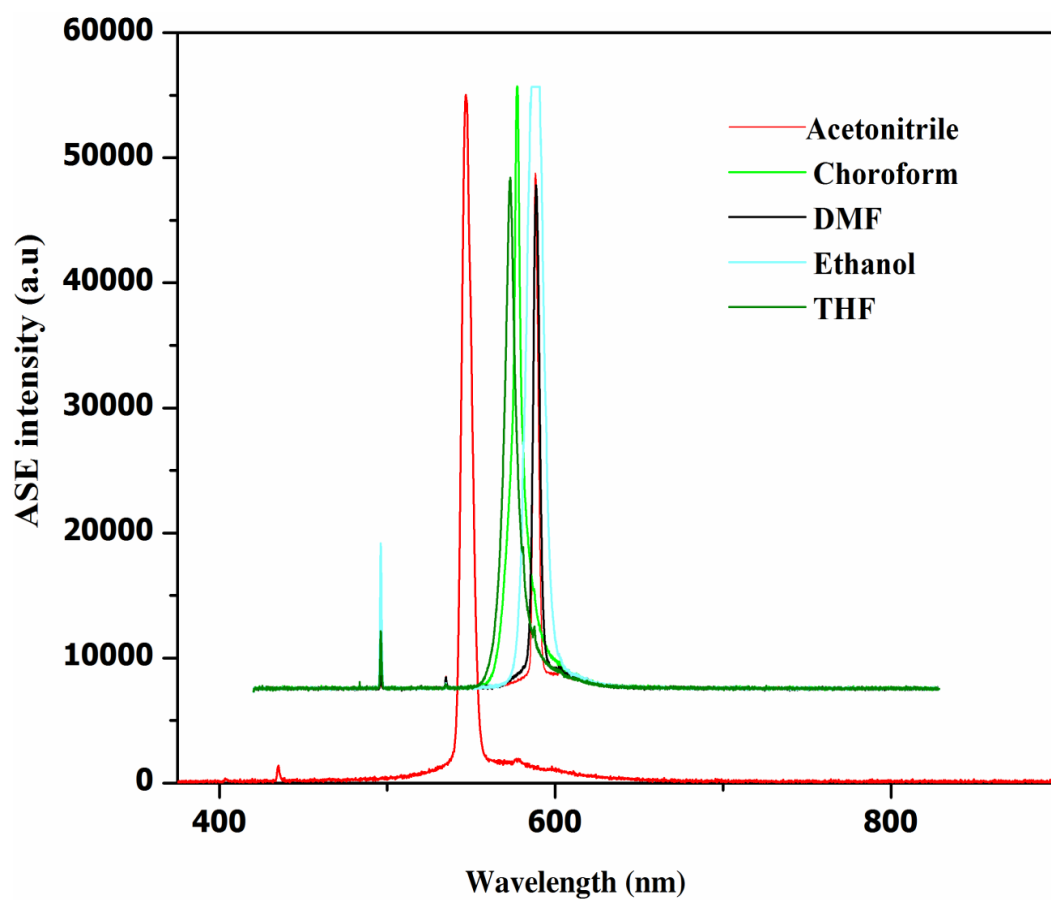
Fig 5.6 ASE spectra of DMAPPP in defined solvent.

5.2.2.3. Dependence of ASE on concentration

Fig.5.7 shows the ASE intensities variation of DMAPPP as a function of the concentration. The concentrations were taken from 2 to 6mM. The solvents were DMF, acetone and THF and the pump power was 9 mJ. It was found that, as the concentration increased, the intensity of the ASE increases for each solution. It was seen that the ASE did not reach saturation even at high concentrations.
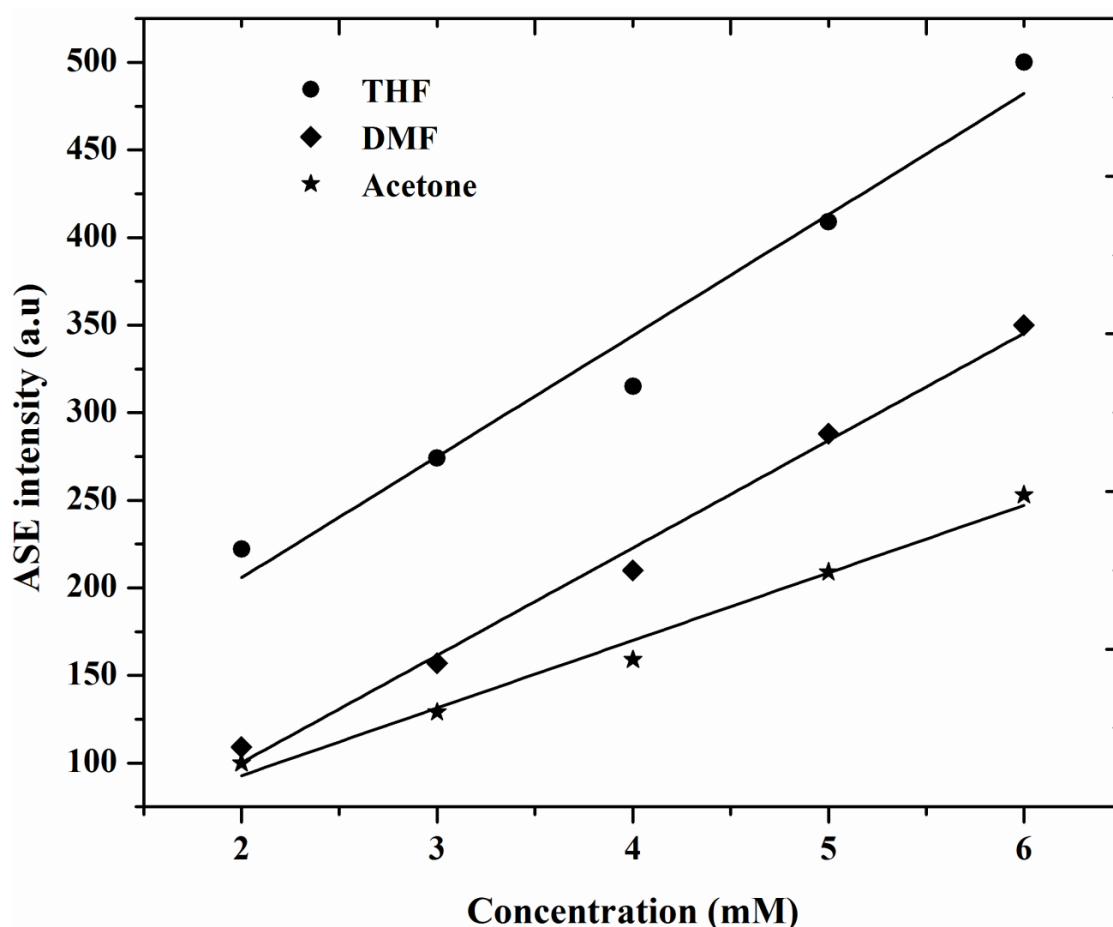
Fig 5.7 ASE intensities of DMAPPP in DMF, acetone and tetrahydrofuran (THF) as a function of a concentration at a concentration of2 to 6mM.

5.2.2.4. Dependence of ASE on Pump Pulse Energy

Fig.5.8 shows the comparison of the ASE intensity of DMAPPP dissolved in different solvents DMF, acetone and THF under identical condition. The concentration was kept at 6mMfor each solution; and the pump power was taken from 3 to 15 mJ. It was found that as the pump power was increased, the intensity of DMAPPP in acetone increased slowly, while in THF the intensity increased rapidly. Here, the solvent plays an important rule for the ASE behavior.
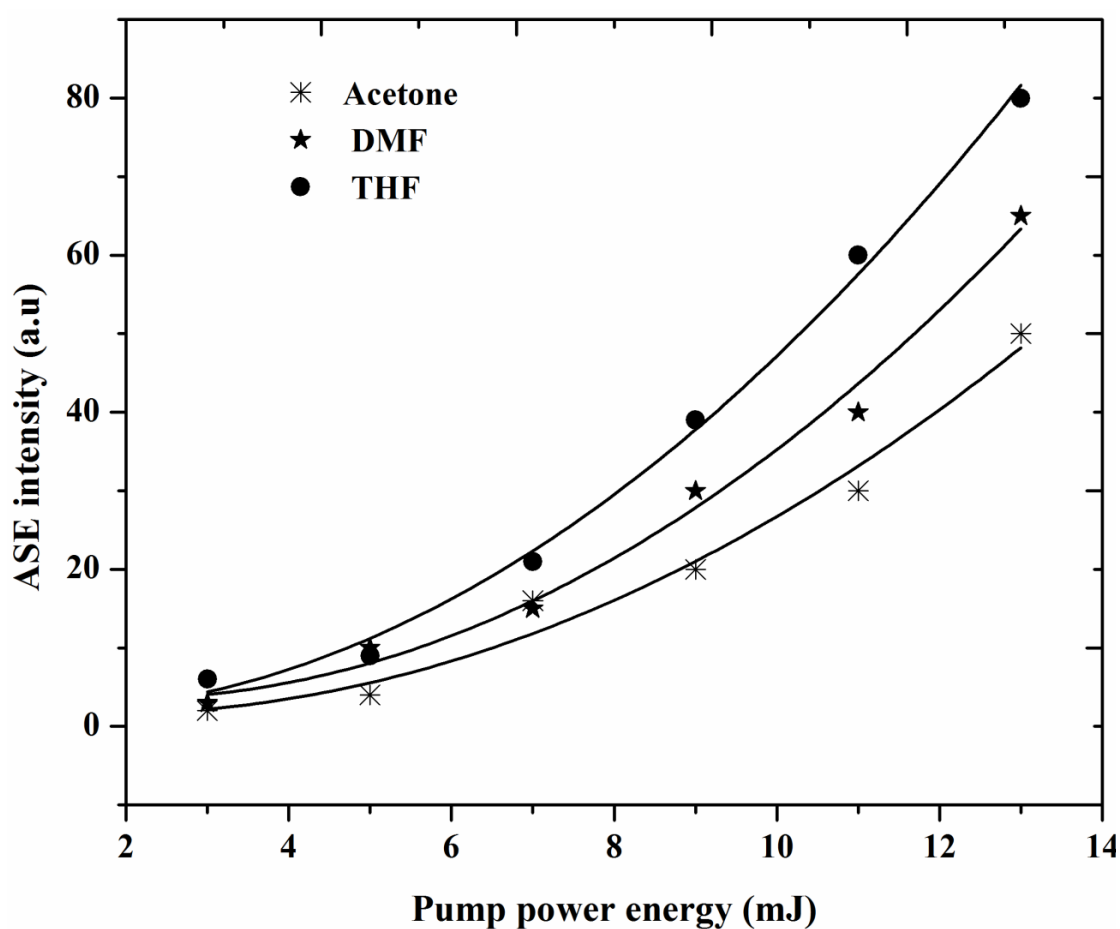
Fig 5.8 ASE intensities of DMAPPP in DMF, acetone and tetrahydrofuran (THF) as a function of pulse energy at a pump power energy of 9 mJ.

5.2.2.5. The Photochemical Stability Measurements

The photochemical stability of DMAPPP in DMF at a concentration of 6.5Mm was examined. These solutions were pumped by the third harmonic (355 nm) of Nd: YAG with pulse energy of 6 mJ and a repetition rate of 10 HZ. After 30000 pulses, the ASE intensity of DMAPPP remained constant, see **Fig.5.9**.
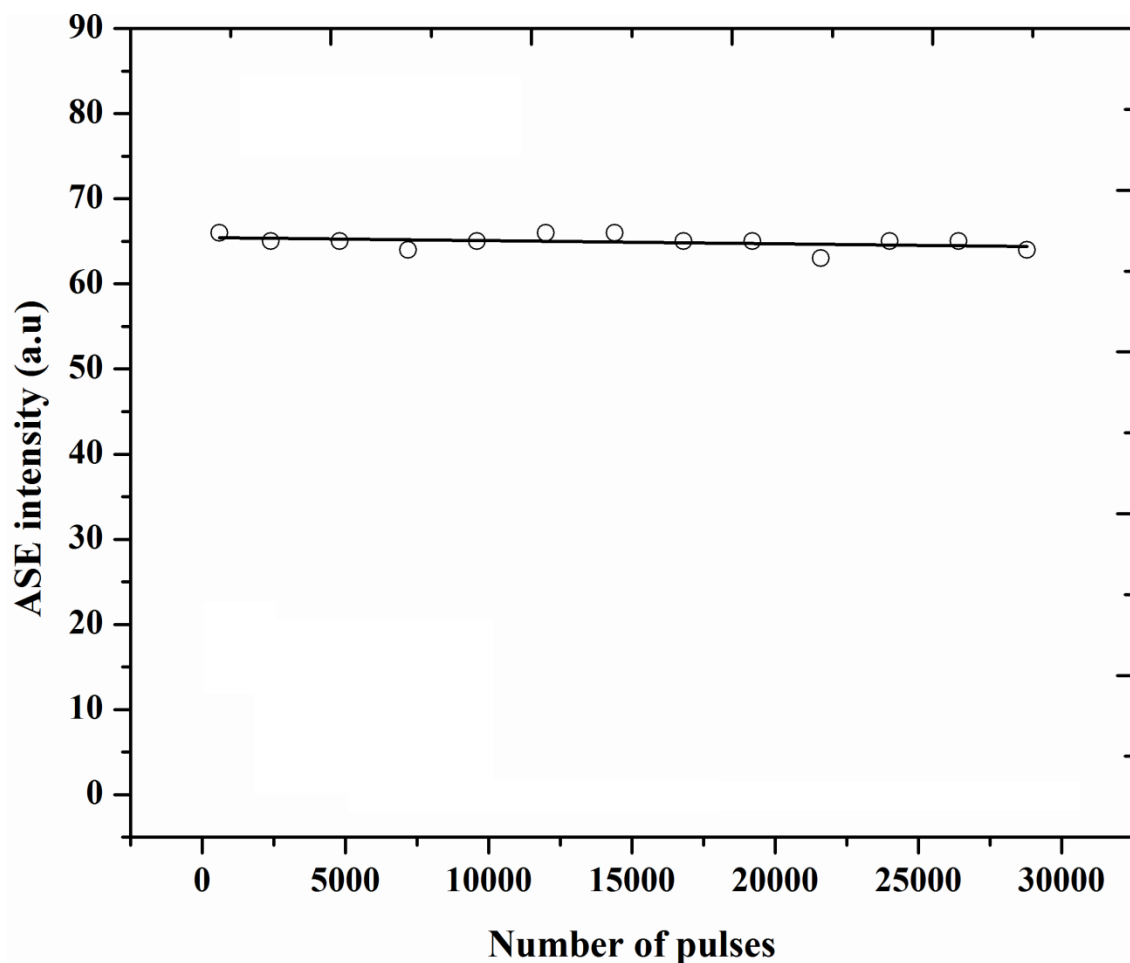
Fig.5.9 The photochemical stability of DMAPP in DMF. The concentration is 6.5mM.

The photochemical stability of DMAPPP in different solvents was studied under the same operating conditions, as mentioned above. After 30000 pulses, the ASE intensity of THF and acetone was dropped to 32% and 25%, respectively as seen in (**Fig.5.10**).
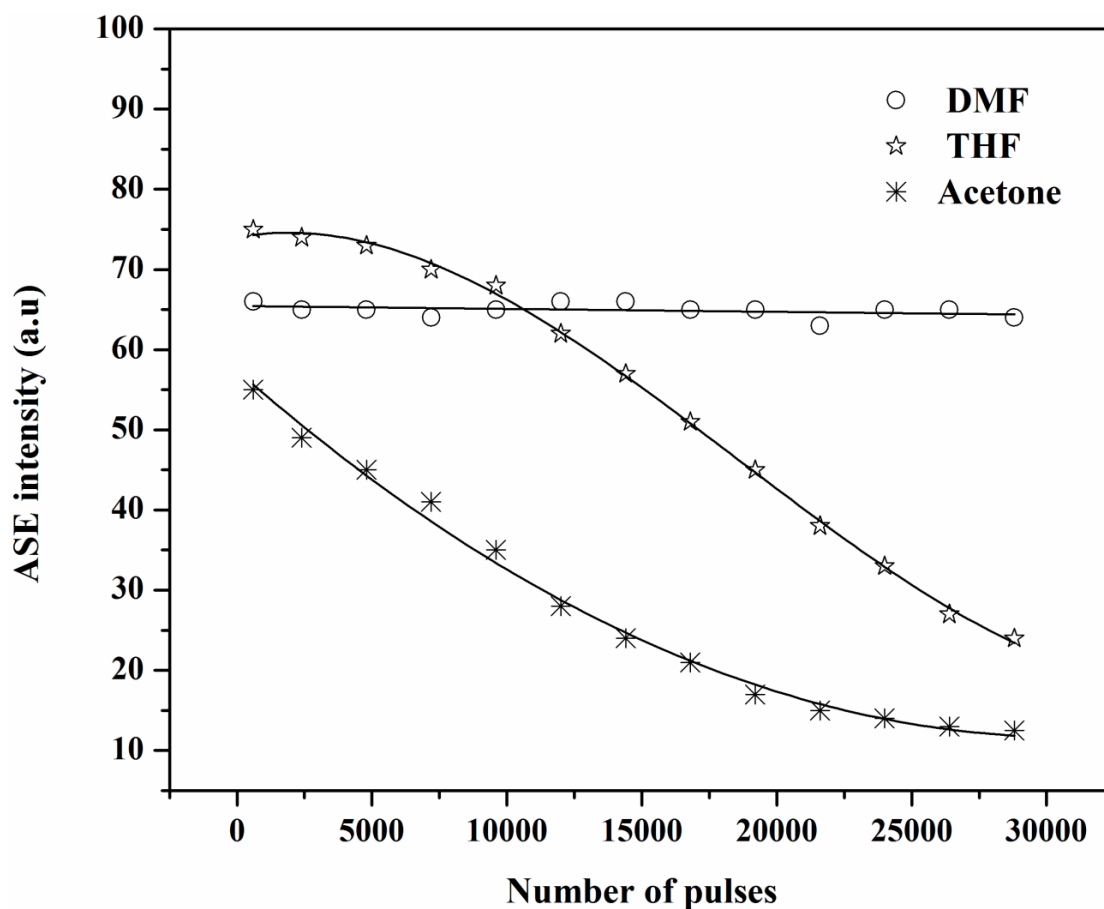
Fig.5.10 The photochemical stability of DMAPPP in different solvents at a concentration of 6Mm.

5.2.2.6. The Gain Measurement

The optical gain of DMAPPP in DMF was measured for the concentration 6mM. The pump pulse energy was varied from 3 mJ to 13 mJ; the excitation wavelength was 355nm. The ASE intensity was measured for two lengths of excitation l_1 =0.5cm and l_2 =0.3cm [110].

$$\frac{I_1}{I_2} = \frac{e^{\gamma l_1}-1}{e^{\gamma l_2}-1} \qquad (5.2)$$

Where: l is the length of excitation and γ is the optical gain.

The results showed that the optical gain of DMAPPP in DMF at concentration of 9 mJ

is 1.8 cm^{-1}. This is perhaps one of the highest gains obtainable from laser dyes [111].

Show **Fig 5.11.**
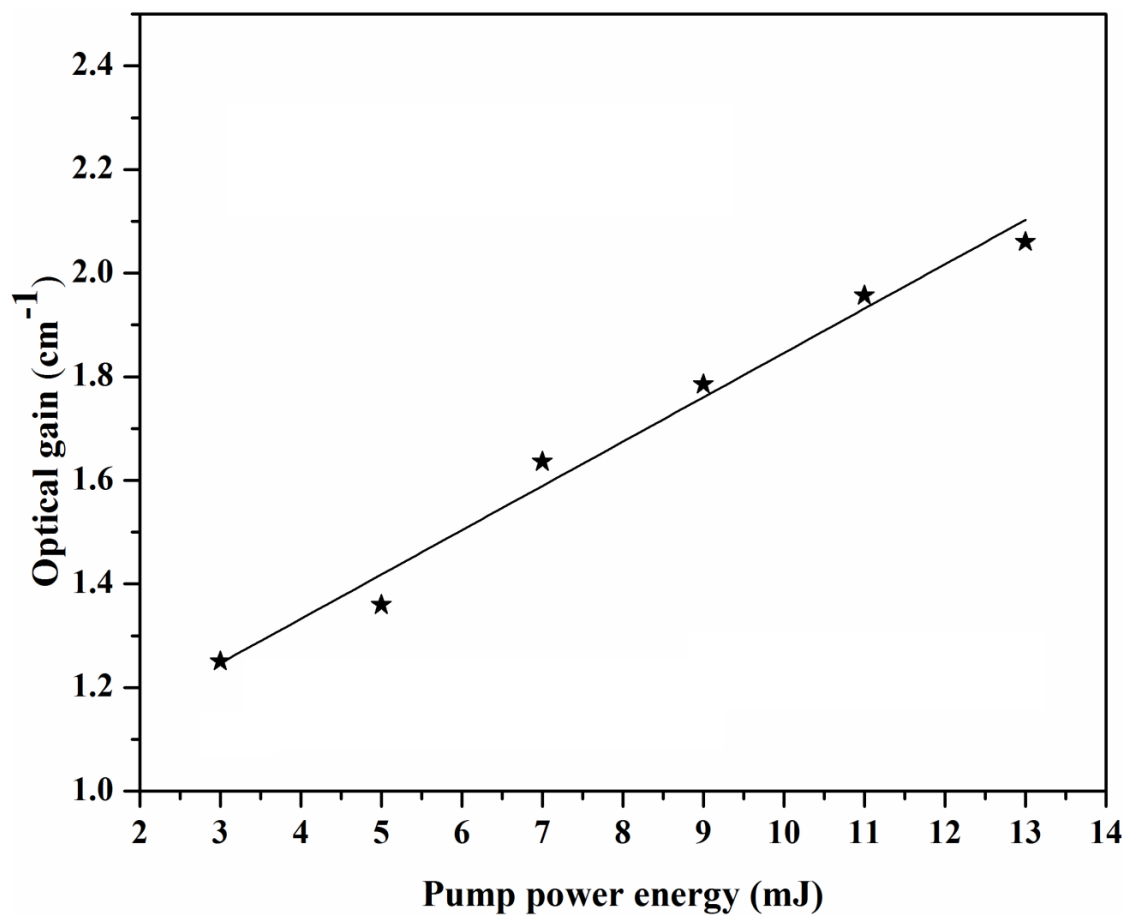
Fig.5.11 The relationship between the optical gains vs. pump pulse energy for
DMAPP in DMF a concentration of 0.6.5mM.

5.3 PART (II)

5.3.1. Spectral properties of MDMAPPand CPDAPP comperd with DMAPPP
5.3.1.1. Absorption of MDMAPP

The steady- state absorption and fluorescence spectra of 1-(4-methylphenyl)-3-(4- N, N-dimethyl amino phenyl)-2-propen-1-one (MDMAPP) in acetone under different concentrations ranging from 0.65 to 6.5mMwere recorded. It showed an absorption band at 405 nm. By increasing the concentration, there was no new absorption peak in the longer wavelength region of the absorption spectra, and the absorption profile remained unchanged. However, the optical density of the band 405 nm increased monotonically when the concentration was increased see **(Fig 5.12)**.
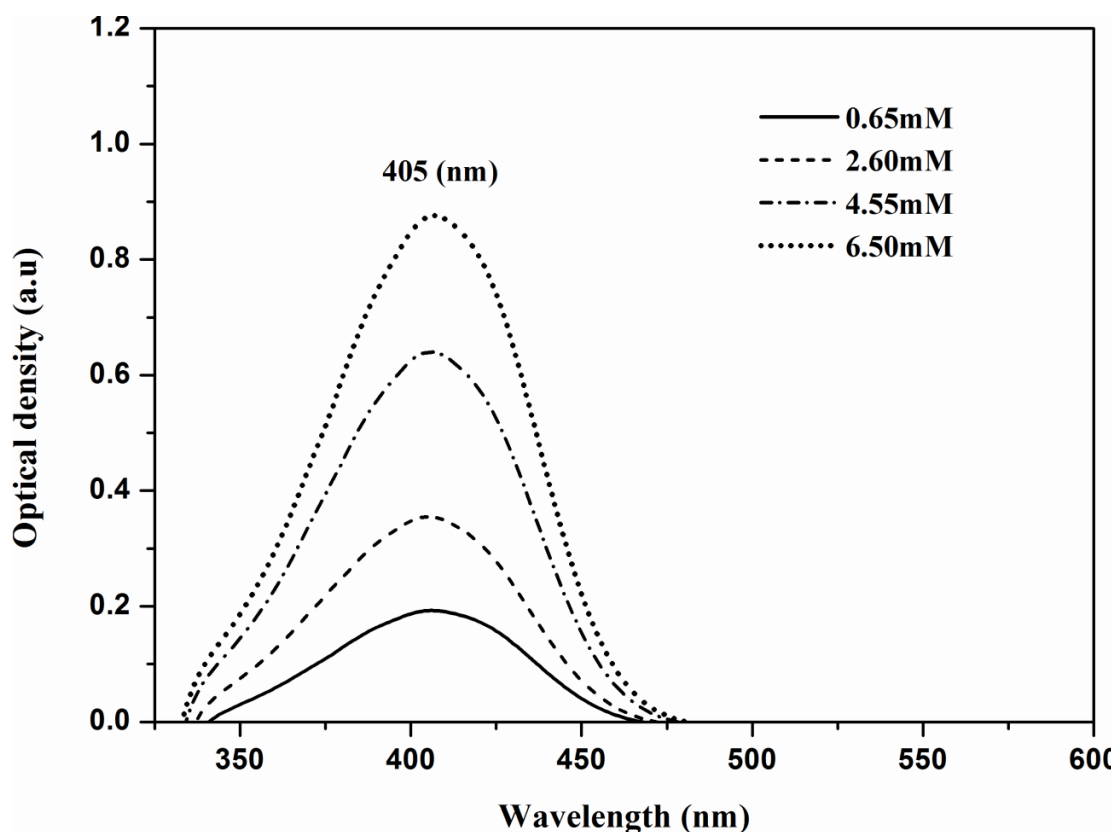
Fig 5.12. Absorption spectra of MDMAPP in acetone for different concentrations from 0.65-6.5 mM.

5.3.1.2. Fluorescence of MDMAPP

The fluorescence spectra of MDMAPP in acetone, for the different concentrations 0.65 – 6.5 mM , were investigated. The results showed only one band at 515 nm, the spectra profile did not change irrespective of concentration for this dye. This indicates that the absence of excimer or exciplex for these dye solutions over all the concentrations used, as illustrated in (**Fig 5.13**). Moreover, the intensity decreased with an increasing the concentration of the dye.
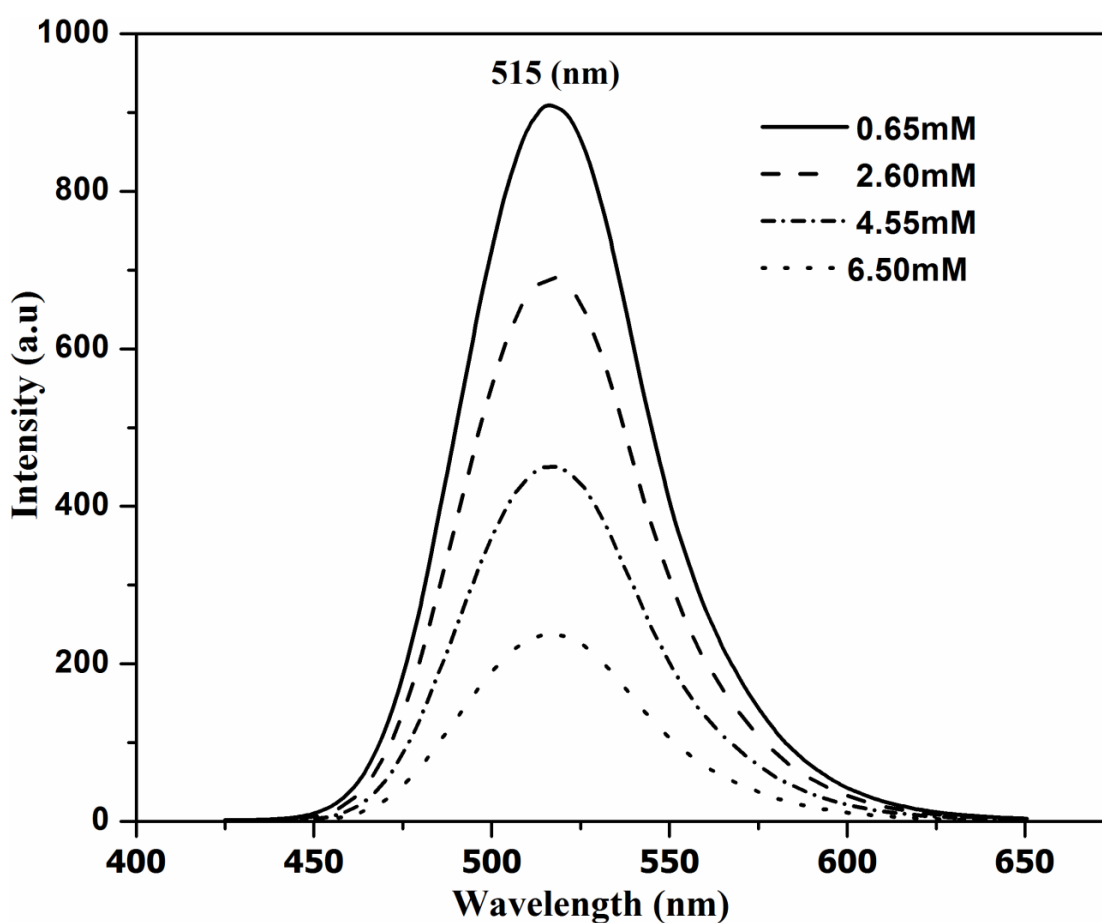
Fig 5.13 Fluorescence spectra of MDMAPP in acetone for different concentrations from 0.65-6.5 mM.

The above results have been compared with the spectral properties of 3-(4-(dimethyl amino)phenyl)-1-phenyl-(2E)-propen-1-one (DMAPPP) as a reference dye.(**Fig 5.1**) **&&** (**Fig 5.2**) shows the absorption and fluorescence spectra of DMAPPP in acetone for different concentrations ranging from 0.65 to 6.5mM. It showed an

absorption band at 405 nm. By increasing the concentration, there was no new absorption peak observed ,whereas, the fluorescence spectra of DMAPPP in acetone under an excitation wavelength of 355 nm for different concentrations (0.65 to 6.5mM) were obtained as shown in **Fig.5.2.** The fluorescence spectra had one band, at 525nm.

The difference between MDMAPP and DMAPPP in their chemical structures is a methyl group attached to *para-position* to ring A. Here the methyl group is acting as electron donors by inductive effect. The addition of methyl group to DMAPPP dye leads to decrease the fluorescence wavelength by 10 nm to blue shift, whereas no significance change in the absorption spectra as expected.

5.3.1.3. Absorption of CPDAPP

The optical properties such as absorption of 1-(4-chloridephenyl)-3-(4- N, N dimethyl amino phenyl)-2-propen-1-one (CPDAPP) dissolved in acetone with different concentrations from 0.65 to 6.5mMwere recorded. The absorption spectra showed only one peak at 420 nm show (**Fig 5.14**). When the concentration was increased, there was no new absorption peak detected in the longer wavelength region.

However, the optical density of the peak 420 nm increased monotonically with concentration.
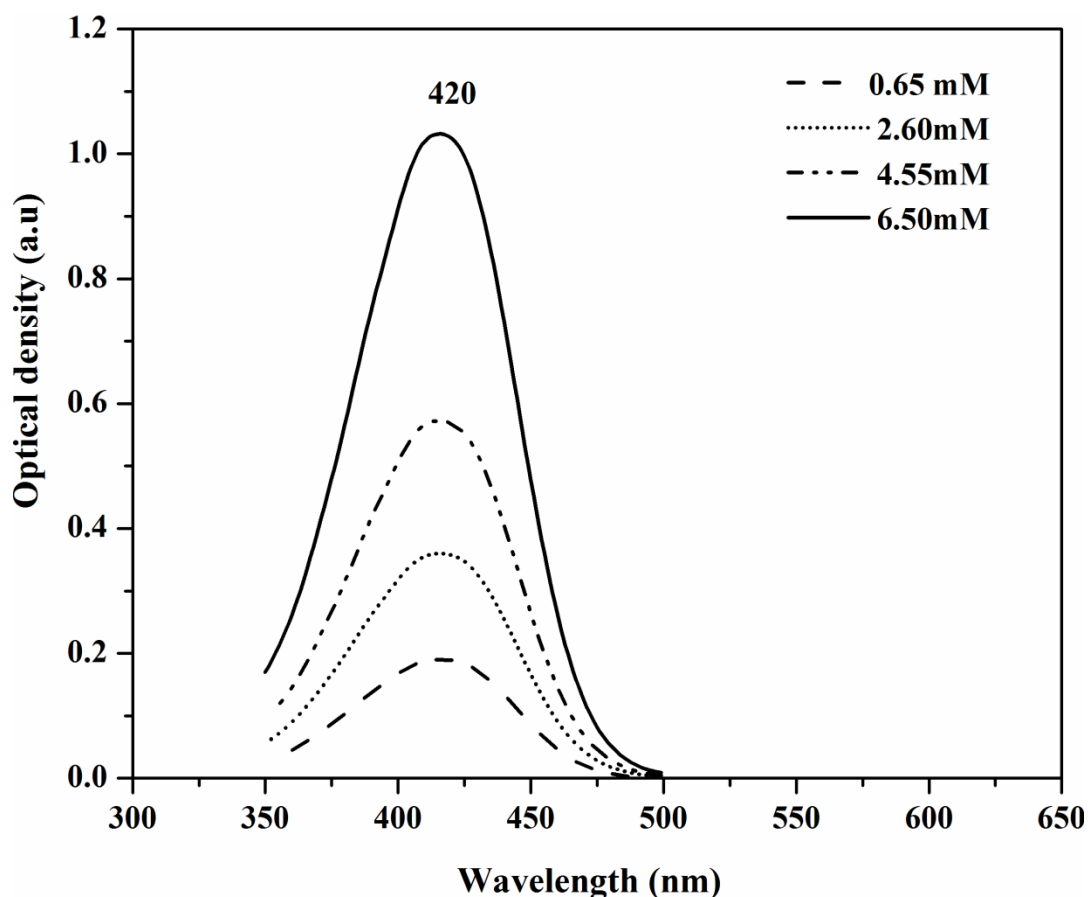
Fig 5.14. Absorption spectra of CPDAPP in acetone for different concentrations from 0.65-6.5 mM.

5.3.1.4. Fluorescence of CPDAPP

The fluorescence spectra of CPDAPP in acetone, for the different concentrations 0.65 – 6.5 mM. Were studded. The results showed only one band at 535 nm, the spectra profile did not change irrespective of concentration for this dye. This indicates that the absence of excimer or exciplex for these dye solutions over all the concentrations used, as illustrated in (**Fig.5.15**). Moreover, the intensity decreased with an increasing the concentration of the dye.
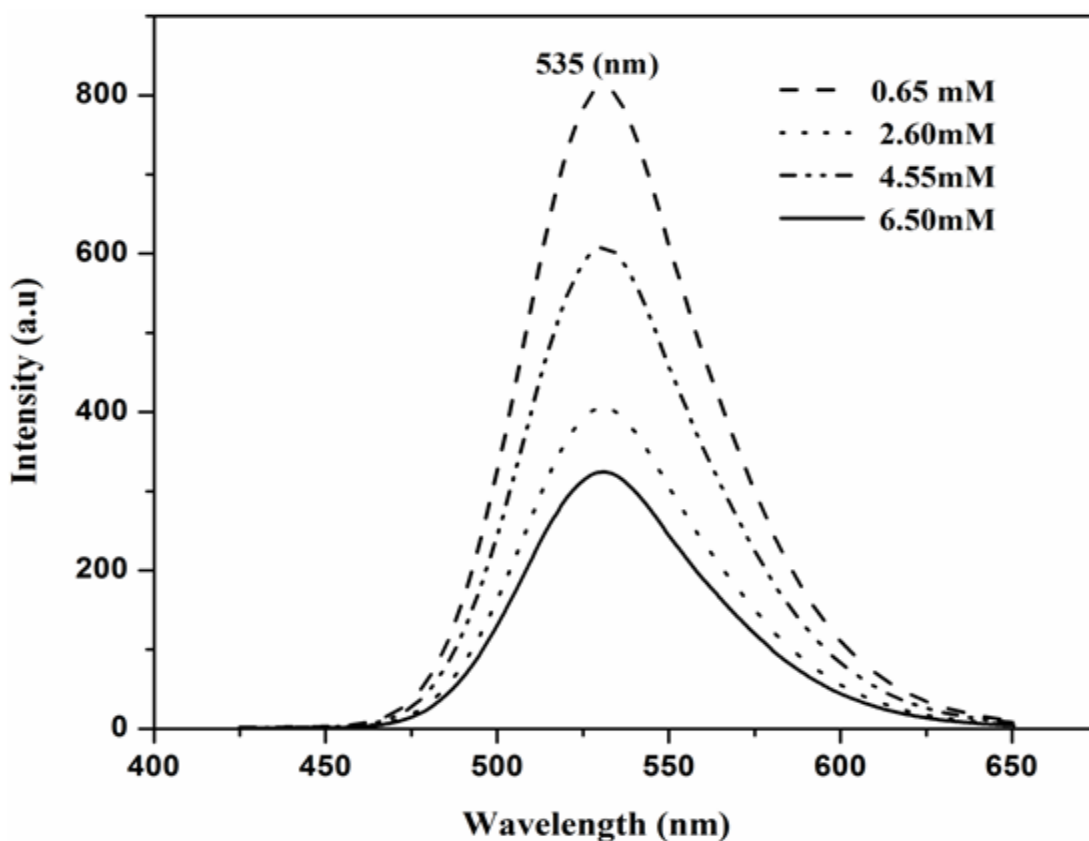
Fig 5.15.Fluorescence spectra of CPDAPP in acetone for different concentrations from 0.65-6.5 mM.

The results obtained were compared with the spectral properties of 3-(4-(dimethyl amino)phenyl)-1-phenyl-(2E)-propen-1-one (DMAPPP).(**Fig 5.1**)& (**Fig 5.2**) shows the absorption and fluorescence spectra of DMAPPP in acetone for different

concentrations ranging from 0.65 to 6.5mM. It showed an absorption band at 405 nm. By increasing the concentration, there was no new absorption peak observed, whereas, the fluorescence spectra of DMAPPP in acetone under an excitation wavelength of 355 nm for different concentrations (0.65 to 6.5mM) were obtained as shown in (**Fig 5.1**). The fluorescence spectra had one band, at 525nm.

The difference between CPDAPP and DMAPPP in their chemical structures is a chlorine group attached to *para-position* to ring A, the chlorine is acting as electron acceptor. The addition of chlorine group to DMAPPP dye leads to increase the fluorescence wavelength by 20 nm to red shift, whereas the absorption peak shifted by 15 nm to the red.

5.3.1.5. Stokes' shift of MDMAPP

MDMAPP was dissolved in various organic solvents that have different dielectric constants. The concentration was kept at 0.65mM. It was observed that there are very small changes in the absorption and fluorescence spectra, the only difference being a small shift in the peaks of the absorption and the fluorescence wavelengths. The Stokes' shift has a linear variation with the dipole factor [87-89].

Fig 5.16 shows a plot of the Stokes' shift as a function of dipole factor for representative solvents, which have been calculated by using equations (3.20) and (3.21). This dipole factor is a measure of dipole-dipole interaction between the solvents and the solute. It could be seen that MDMAPP is slightly less polar than DMAPPP. These results indicate that all of these dyes display great variations in the dipole moment in the excited state.

Table.5.5: Stokes' shift of MDMAPP

Solvent	Dielectric constant (ε)	refractive index (n)	Dipole factor	DMAPMPP λ max		DMAPMPP ν		
				Absorption	Fluorescence	$\nu_{Absorption}$ (nm-1)	$\nu_{Fluorescence}$ (nm-1)	$\nu_{Absorption-Fluorescence}$ (cm-1)
Benzene	2.27	1.5011	0.001642	406	473	0.002463	0.002114	3490
Toluene	2.38	1.4969	0.013235	404	477.5	0.002475	0.002094	3810
Chloroform	4.81	1.4458	0.148295	418	508.5	0.002392	0.001967	4260
Acetic acid	6.15	1.3716	0.202174	427	511.5	0.002342	0.001955	3870
(THF)	7.58	1.4072	0.209572	403	503	0.002481	0.001988	4930
Acetone	20.7	1.3587	0.284307	404	515.5	0.002475	0.00194	5350
Ethanol	24.5	1.3614	0.288687	421	533	0.002375	0.001876	4990
Methanol	32.7	1.3284	0.308587	413	531	0.002421	0.001883	5380
DMF	36.7	1.4305	0.27438	415	527.5	0.00241	0.001896	5140
Acetonitrile	37.5	1.3441	0.305416	410	528.5	0.002439	0.001892	5470
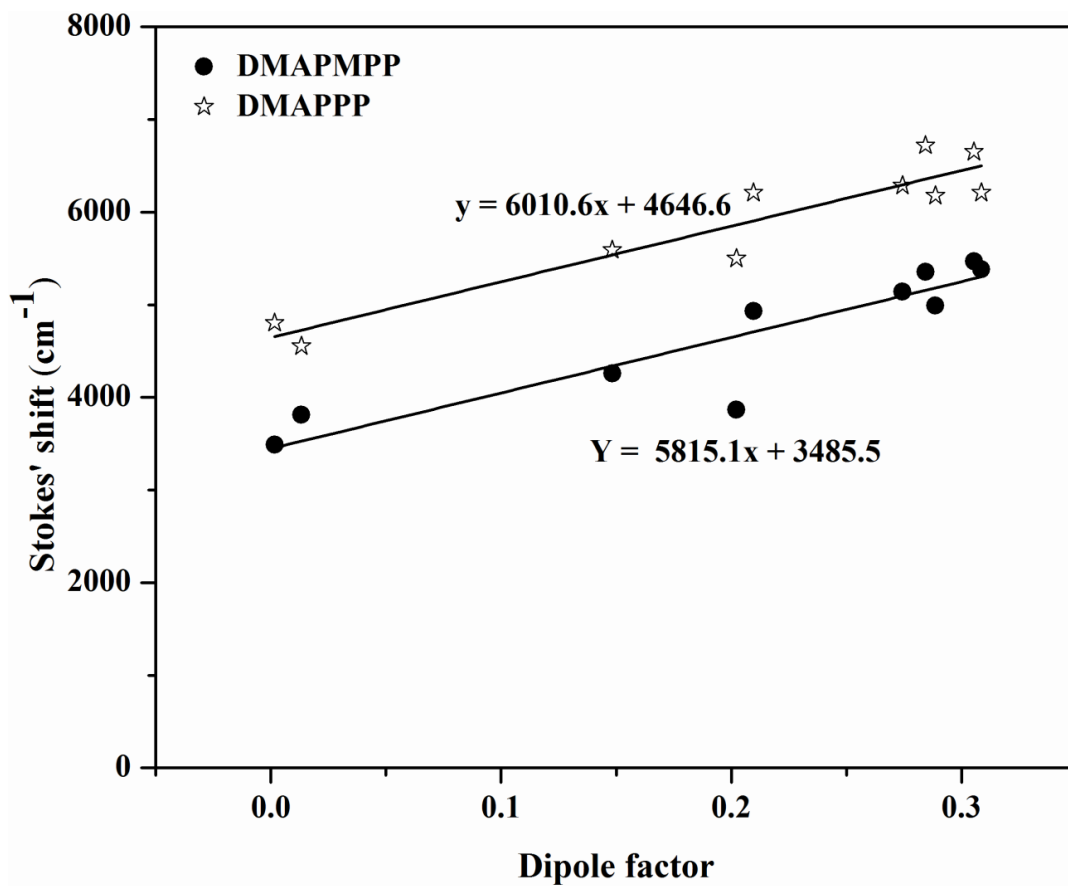
Fig 5.16 Variation in the Stokes' shift of MDMAPP and DMAPPP in solution with a dipole factor for different solvents .

5.3.1.6. Stokes' shift of CPDAPP

CPDAPP was dissolved in various organic solvents that have different dielectric constants. The concentration was kept at 0.65mM. It was observed that there are very small changes in the absorption and fluorescence spectra, the only difference being a small shift in the peaks of the absorption and the fluorescence wavelengths. The Stokes' shift has a linear variation with the dipole factor [87-89].

Fig 5.17 shows a plot of the Stokes' shift as a function of dipole factor for representative solvents, which have been calculated by using equations (3.20) and (3.21). This dipole factor is a measure of dipole-dipole interaction between the solvents and the solute. It could be seen that CPDAPP is slightly less polar than DMAPPP. These results indicate that all of these dyes exhibit large changes in the dipole moment in the excited state.

Table.5.6: Stokes' shift of MDMAPP

Solvent	Dielectric constant (ε)	refractive index (n)	Dipole factor	CPDAPP λ max		CPDAPP ν		
				Absorption	Fluorescence	ν Absorption (nm-1)	ν Fluorescence (nm-1)	ν Absorption $-$ Fluorescence (cm-1)
Benzene	2.27	1.5011	0.001642	420	487.5	0.002381	0.002051	3300
Toluene	2.38	1.4969	0.013235	413	480	0.002421	0.002083	3380
Chloroform	4.81	1.4458	0.148295	424	521.5	0.002358	0.001918	4410
Acetic acid	6.15	1.3716	0.202174	429	520.5	0.002381	0.001869	5120
Tetrahydrofuran	7.58	1.4072	0.209572	413	516	0.002421	0.001938	4830
Acetone	20.7	1.3587	0.284307	418	532	0.002392	0.00188	5130
Ethanol	24.5	1.3614	0.288687	425	542	0.002353	0.001845	5080
Methanol	32.7	1.3284	0.308587	427	544	0.002342	0.001838	5040
Dimethylformamide	36.7	1.4305	0.27438	427	541.5	0.002342	0.001845	4970
Acetonitrile	37.5	1.3441	0.305416	417	537	0.002398	0.001862	5360
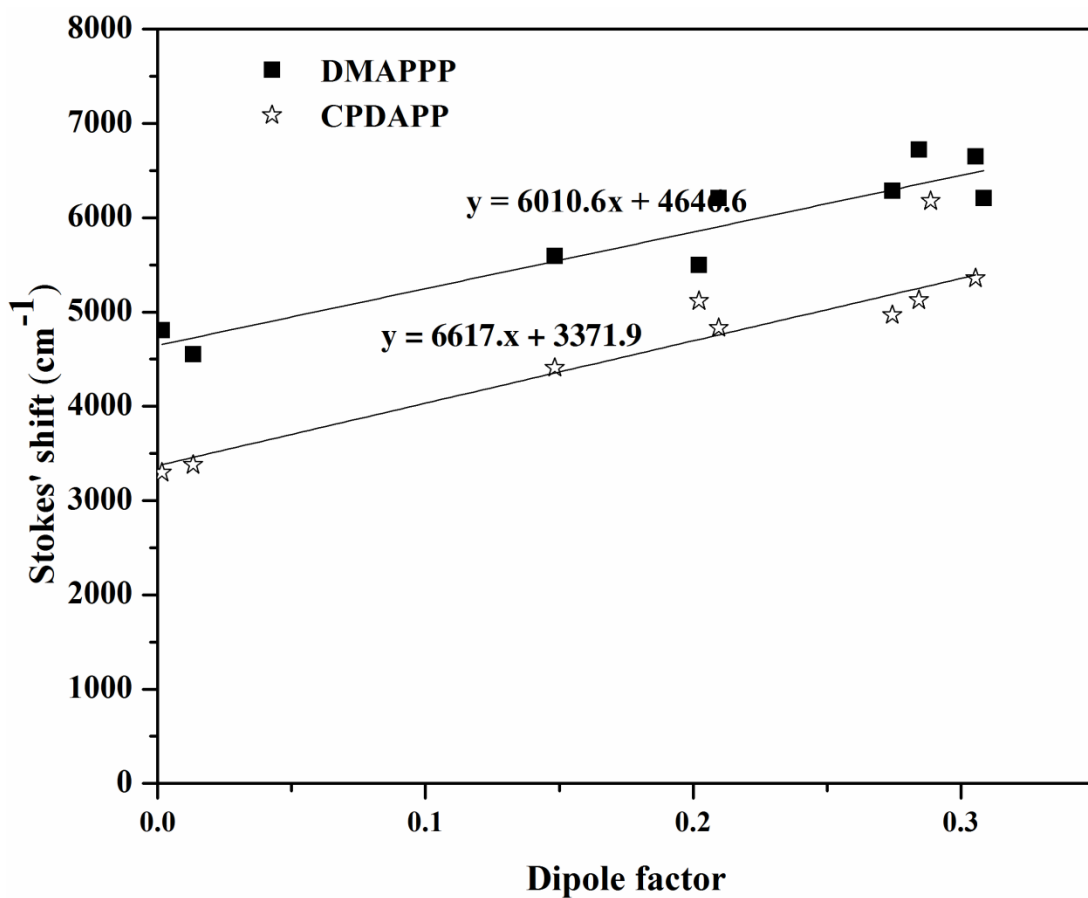
Fig 5.17 Variation in the Stokes' shift of CPDAPP and DMAPPP in solution with a dipole factor for different solvents.

5.3.1.7. Quantum yield of fluorescence from MDMAPP

Rhodamine 6G (Rh 6G) in methanol has a known fluorescence quantum yield (Φ_F) of 0.94. Rh 6G in methanol at a concentration of 0.65mM of was taken as the standard for measurement of quantum yields for MDMAPP in different solvents. The quantum yield can be measured using known equation [28].

The fluorescence spectra of MDMAPP in different organic solvents were recorded. The concentration was kept at 0.65mM. The fluorescence spectra were recorded at the excitation wavelength of 355 nm. The quantum yield of these solutions was calculated as seen in the table.1a. The results obtained were compared with the quantum yield of DMAPPP (**see table 5.4**). The results showed that the quantum yield depends on the solvent and the chemical structure of the dye.

Table.5.7 shows the quantum yields of fluorescence (Φ_F) for DMAPPP and MDMAPP.

Solvent	Dielectric constant (ε)	ϕ_F DMAPPP	ϕ_F MDMAPP
Benzene	2.27	0.27	0.13
Toluene	2.38	0.24	0.11
Chloroform	4.81	0.66	0.89
Acetic acid	6.15	0.05	0.20
Tetrahydrofuran	7.58	0.96	0.86
Acetone	20.7	0.88	0.66
Ethanol	24.5	0.37	0.44
Methanol	32.7	0.02	0.22
Dimethylformamide	36.7	0.93	0.96
Acetonitrile	37.5	0.66	0.40

5.3.1.8. Quantum yield of fluorescence from CPDAPP

Rhodamine 6G (Rh 6G) in methanol has a known fluorescence quantum yield (Φ_F) of 0.94. Rh 6G in methanol at a concentration of 0.65mM of was taken as the standard for measurement of quantum yields for CPDAPP in different solvents. The quantum yield can be measured using known equation [20].

The fluorescence spectra of CPDAPP in different organic solvents were recorded. The concentration was kept at 0.65mM. The fluorescence spectra were recorded at the excitation wavelength of 355 nm. The quantum yield of these solutions was calculated as seen (**Table 5.5**).The results obtained was compared with the quantum yield of DMAPPP. The results showed that the quantum yield depends on the solvent and the chemical structure of the dye.

Table.5.8 shows the quantum yields of fluorescence (Φ_F) for DMAPPP and CPDAPP.

Solvent	Dielectric constant (ε)	ϕ_F DMAPPP	ϕ_F CPDAPP
Benzene	2.27	0.27	0.13
Toluene	2.38	0.24	0.11
Chloroform	4.81	0.66	0.89
Acetic acid	6.15	0.05	0.20
Tetrahydrofuran	7.58	0.96	0.86
Acetone	20.7	0.88	0.66
Ethanol	24.5	0.37	0.44
Methanol	32.7	0.02	0.22
Dimethylformamide	36.7	0.93	0.96
Acetonitrile	37.5	0.66	0.40

5.3.2 Amplified spontaneous emission (ASE)

5.3.2.1 Amplified spontaneous emission (ASE) of MDMAPP

To study the ASE properties of MDMAPP under high power laser excitation; MDMAP P was dissolved in acetone, the concentration fixed at 1 mM. This solution was transversely excited with a UV laser at 355 nm. At a pump power of 3 mJ, the ASE spectrum was noted. This was the minimum concentration and pump power excitation for MDMAPP to produce an ASE spectrum at 520 nm with a full width at half maximum (FWHM) of 5 nm as shown in **Fig 5.18**. At higher concentrations and similar operational conditions, the ASE spectrum did not change. Note the one-to- one correspondence between the steady-state fluorescence shown in **Fig 5.18** .The results obtained were compared with that DMAPPP under the same operating conditions as shown in **Fig 5.18**. Focusing our attention on MDMAPP (**Fig 4.2b**) DMAPPP (**Fig 4.1a**), these are almost have same chemical structure with difference substitution in the fourth position. Whereas we have a methyl group in the fourth position of MDMAPP, this difference has shifted the ASE of MDMAPP10 nm to the blue region with regard to DMAPPP.
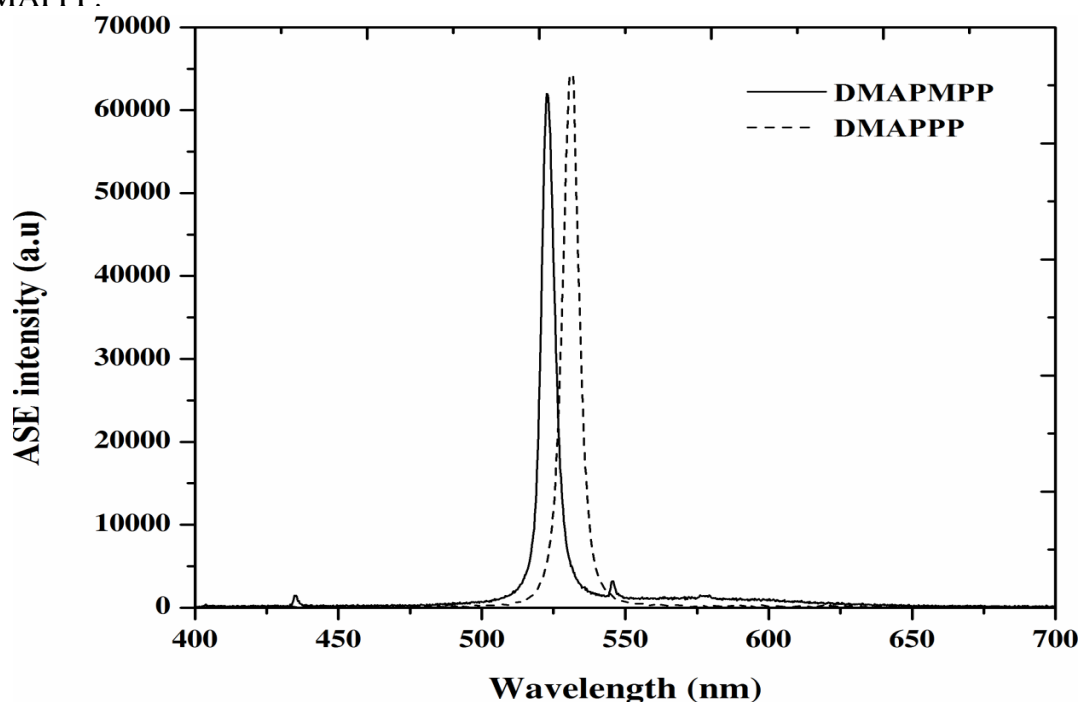
Fig 5.18 ASE spectra of MDMAPP and DMAPPP in acetone at a concentration 1mM.

The ASE spectra of MDMAPP and DMAPPP dissolved in different solvents under identical conditions; the concentration and pump power were kept at 6.5mM and 9 mJ for each solution, respectively (**see table.5.6**). The ASE in acetic acid, methanol, benzene and toluene was not detected even at high pump power energy and concentration. In toluene and benzene this may be due to the lowest solubility of the MDMAPP for these solvents. The absence of the ASE spectra in acetic acid may be due to the protonation of N-dimethylamino group of MDMAPP with responsible for their photo properties. Here the methanol could play similar role by deactivation of the lone pair of N-dimethylamino group by hydrogen bonding; this slightly appears in ethanol which gives poor ASE.

Table5.9 shows The ASE spectra of MDMAPP and DMAPPP in different solvents.

Solvent	Dielectric constant (ε)	λ_{max} MDMAPP	λ_{max} DMAPPP
Benzene	2.27	----	----
Toluene	2.38	----	----
Chloroform	4.81	513	524
Acetic acid	6.15	----	----
Tetrahydrofuran	7.58	511	516
Acetone	20.7	522.5	532
Ethanol	24.5	548	542
Methanol	32.7	----	----
Dimethylformamide	36.7	541	548
Acetonitrile	37.5	544	547

5.3.2.2 Amplified spontaneous emission (ASE) of CPDAPP

To study the ASE properties of CPDAPP under high power laser excitation; CPDAPP was dissolved in acetone, the concentration fixed at 1 mM. This solution was transversely excited with a UV laser at 355 nm. At a pump power of 3 mJ, the ASE

spectrum was recorded. Note that this was the minimum concentration and the minimum pump power excitation for CPDAPP to produce an ASE spectrum at 550 nm with a full width at half maximum (FWHM) of 6 nm as shown in (**Fig 5.19**). At higher concentrations, under identical operational conditions, the ASE spectrum did not change. Note the one-to- one correspondence between the steady-state fluorescence shown in (**Fig 5.2**) and the ASE spectrum, also shown in (**Fig 5.19**). The results obtained were compared with that DMAPPP under the same operating conditions. It was found that the ASE of CPDAPP in acetone was shifted 20 nm to the red region with regard to DMAPPP. This could be due the effect of the chlorine group of CPDAPP.
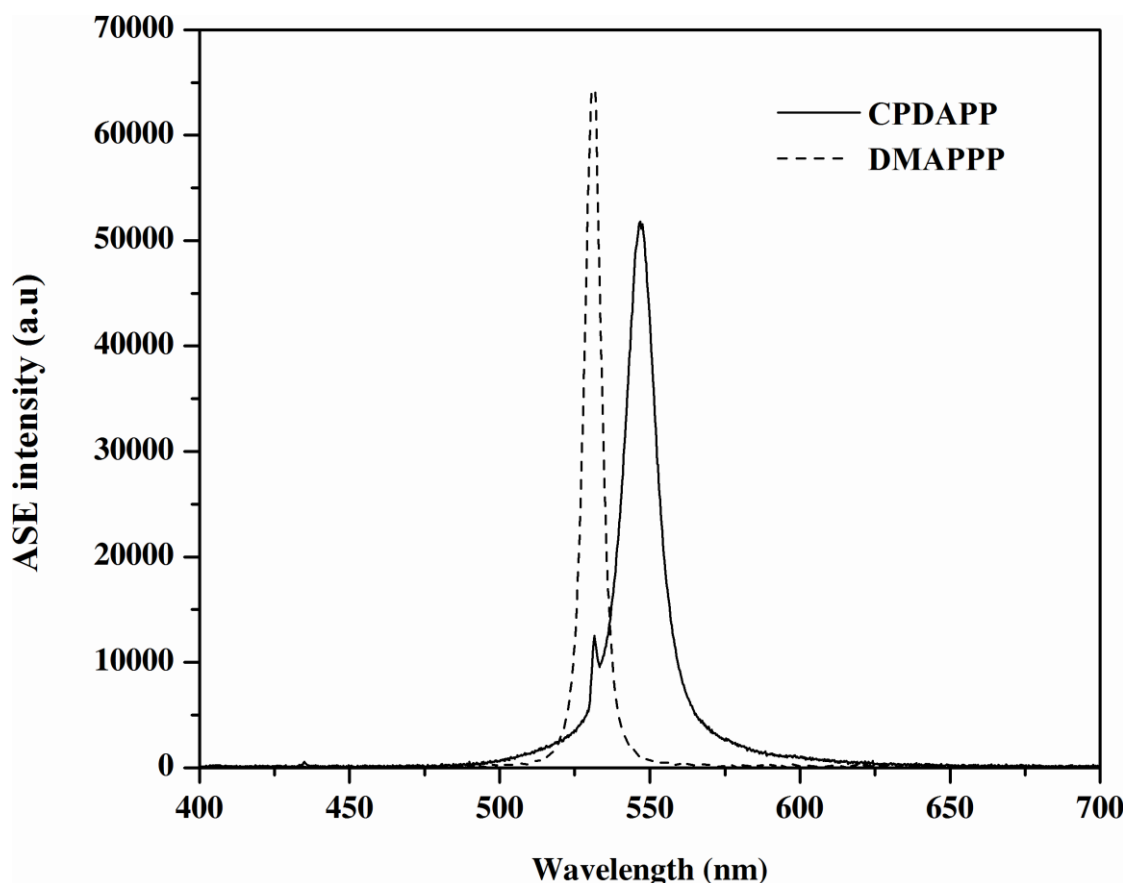
Fig 5.19 ASE spectra of CPDAPP and DMAPPP in acetone at a concentration of1mM.

The ASE spectra of CPDAPP and DMAPPP dissolved in different solvents under identical conditions; the concentration and pump power were kept at 6.5mM and 9 mJ for each solution, respectively. The ASE in acetic acid, methanol, benzene and toluene was not detected even at high pump power energy and concentration. In toluene and benzene this may be due to the lowest solubility of the CPDAPP and DMAPPP. The absence of the ASE spectra in acetic acid could be attributed to the protonation of N-dimethylamino group of CPDAPP and DMAPPP with responsible for their photo properties. For CPDAPP and DMAPPP in methanol, the ASE was not observed. This may be the solvent plays similar role by deactivation of the lone pair of N-dimethylamino group by hydrogen bonding. On the other hand, CPDAPP in chloroform the ASE was not noted nevertheless DMAPPP in chloroform gives highly intense ASE, this refers to the chlorine group in CPDAPP.

Table5.6 shows The ASE spectra of CPDAPP and DMAPPP in different solvents.

Solvent	Dielectric constant (ε)	λ_{max} CPDAPP	λ_{max} DMAPPP
Benzene	2.27	----	----
Toluene	2.38	----	----
Chloroform	4.81	----	524
Acetic acid	6.15	----	----
Tetrahydrofuran	7.58	538	516
Acetone	20.7	547	532
Ethanol	24.5	----	542
Methanol	32.7	----	----
Dimethylformamide	36.7	566	548
Acetonitrile	37.5	563	547

5.3.2.3. The ASE of DMAPPP and MDMAPP Depend the concentration

The variation in the ASE intensities of MDMAPP and MDMAPP dissolved in tetrahydrofuran (THF), with the concentration from 2 to 6mM (**Fig 5.20**). The pump power was fixed at 9 mJ. It was found that as the concentration increased the intensity of the ASE increases for each solution. However, ASE did not reach saturation even at high concentrations.
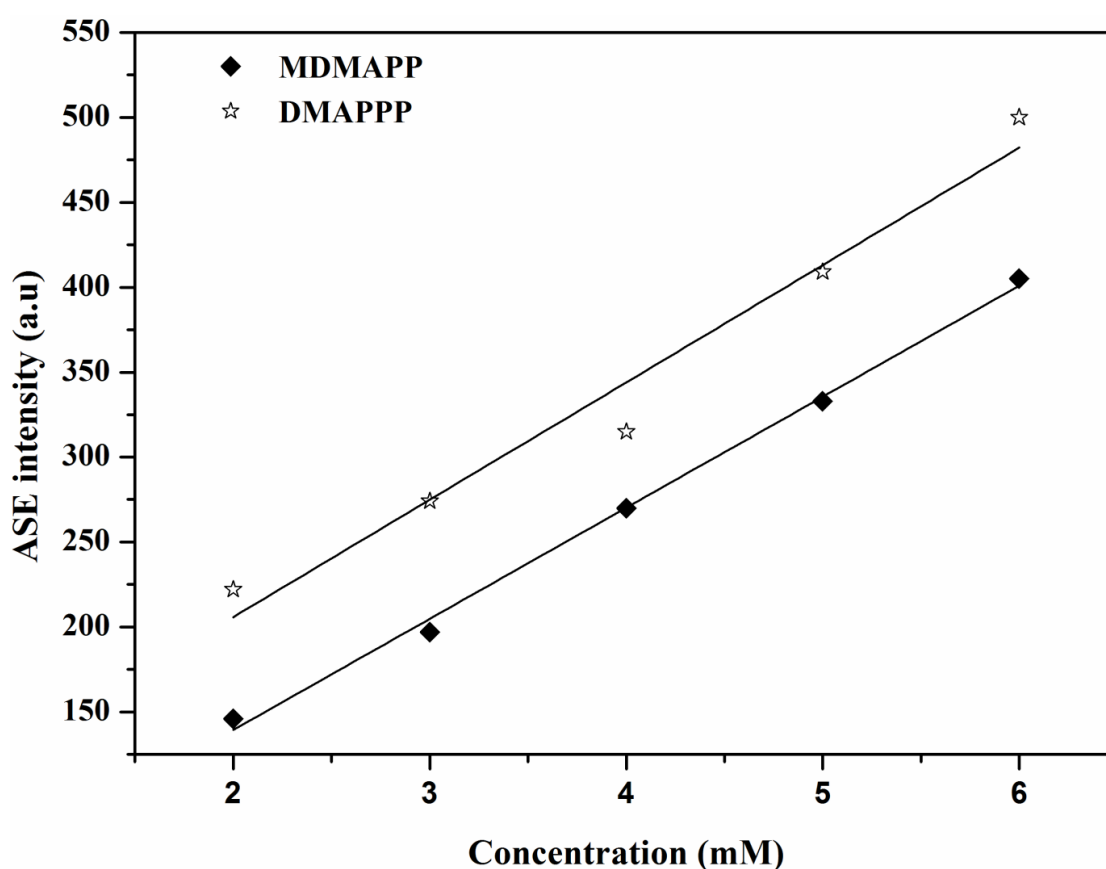
Fig 5.20 ASE intensities of MDMAPP and DMAPPP in THF as a function of the concentration

5.3.2.4. The ASE of DMAPPP and CPDAPP Depend the concentration

The ASE intensity of CPDAPP and DMAPPP in DMF were compared as shown in **Fig 5.21**. The concentration was kept at 6mM for each dye; and the pump power was taken from 3 to 15 mJ. It was found that as the pump power was increased, the ASE intensity of CPDAPP and DMAPPP increases.
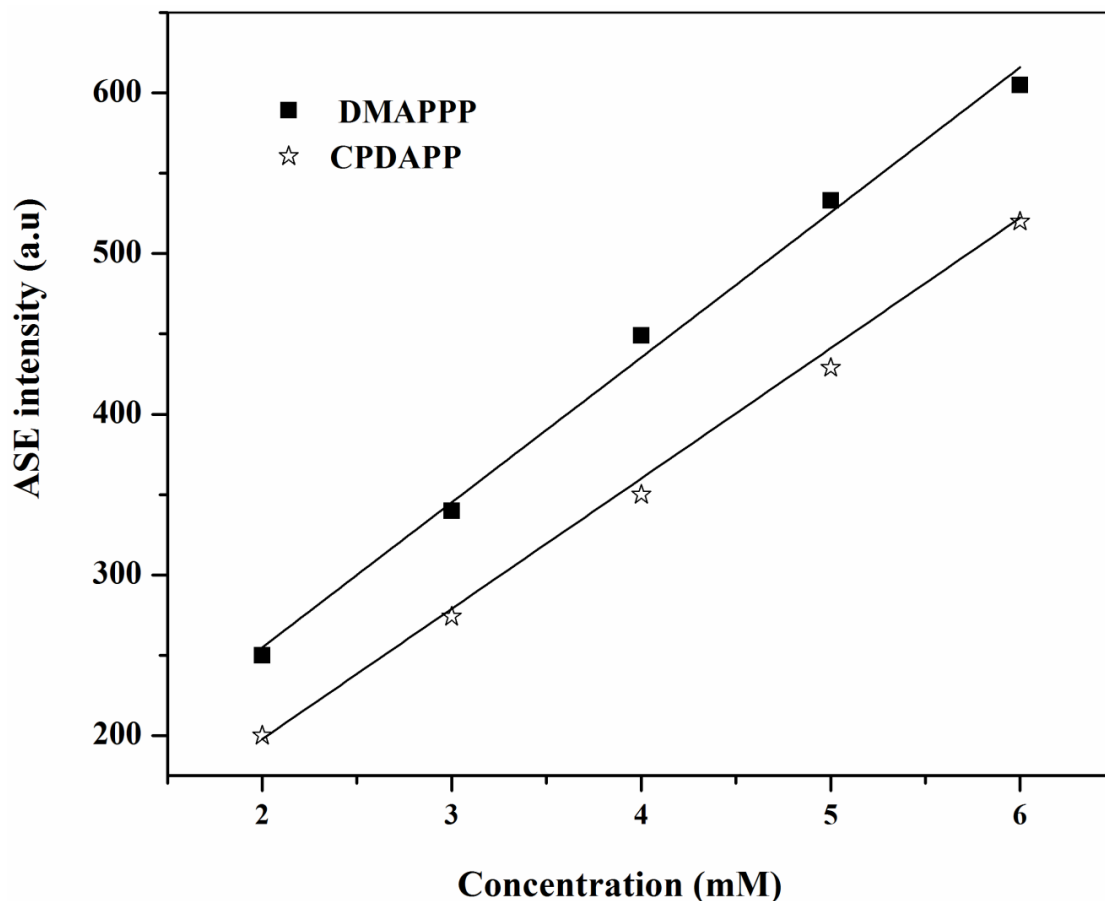
Fig 5.21 ASE intensities of CPDAPP and DMAPPP in THF as a function of the concentration

5.3.2.5. Dependence of ASE from DMAPPP and MDMAPP on the Pump Power

The comparison of the ASE intensity of MDMAPP and DMAPPP in THF under identical condition illustrated (**Fig 5.22**). The concentration was kept at 6mM for each solution; and the pump power was taken from 3 to 15 mJ. It was found that as the pump power was increased, the intensity of DMAPPP in acetone increased slowly, while in THF the intensity increased rapidly.
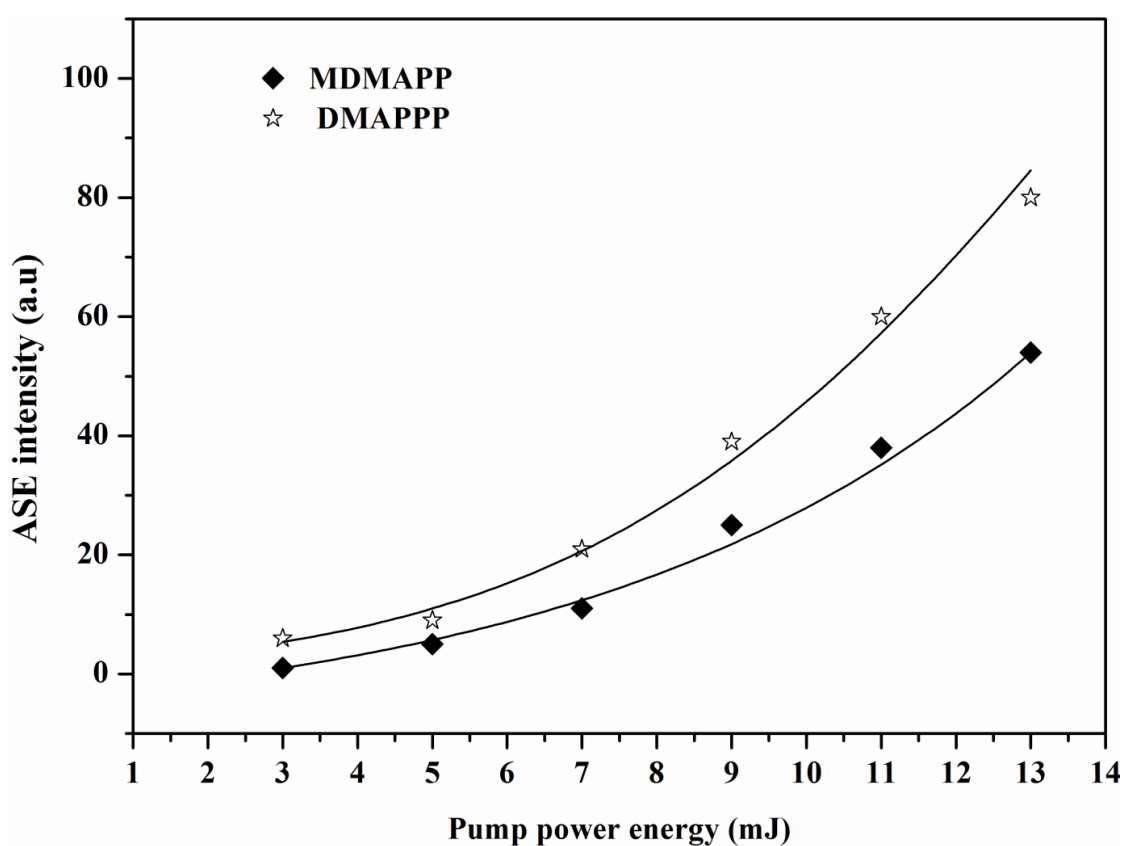
Fig 5.22 ASE intensities of MDMAPP and DMAPPP in THF as a function of pulse energy at a concentration of 6 mM .

5.3.2.6. Dependence of ASE from CPDAPP and MDMAPP on the Pump Power

The comparison of the ASE intensity of CPDAPP and DMAPPP in DMF illustrated (**Fig 5.23**). The concentration was kept at 6mM for each dye; and the pump power was taken from 3 to 15 mJ. It was found that as the pump power was increased, the ASE intensity of CPDAPP and DMAPPP increases.
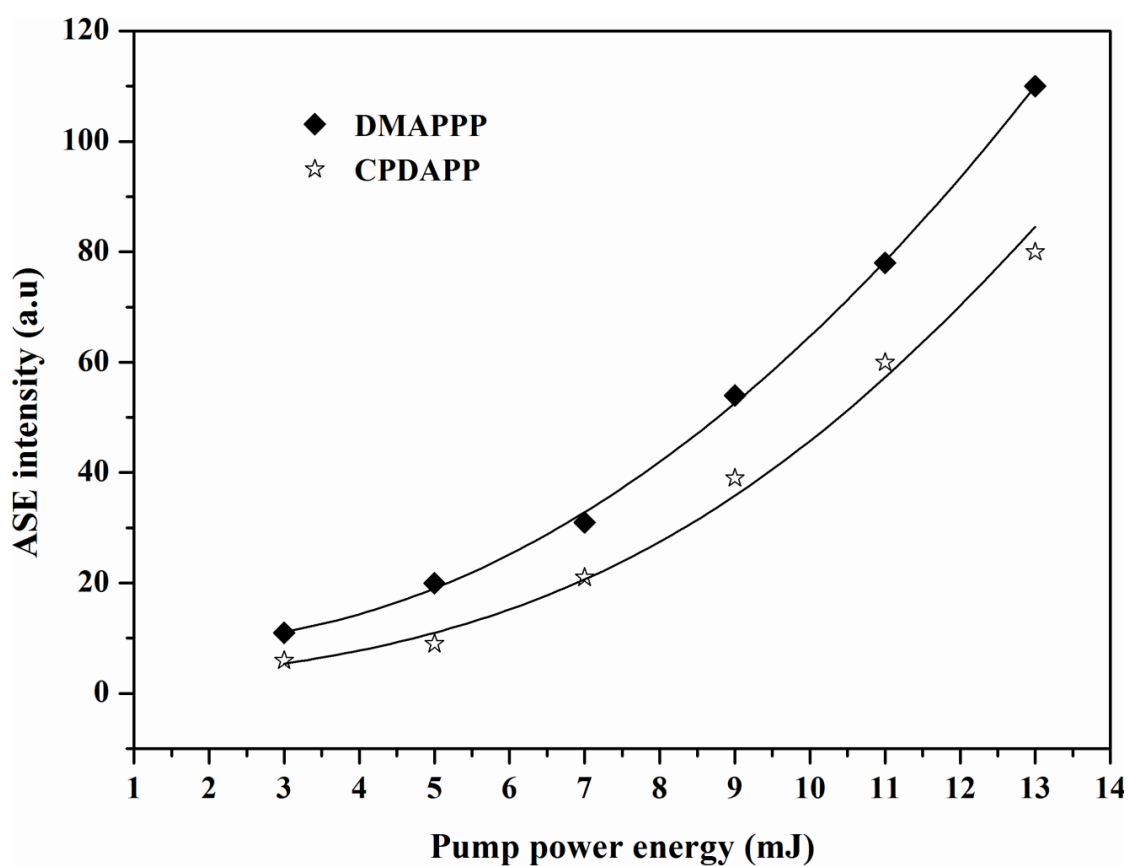
Fig 5.23 ASE intensities of CPDAPP and DMAPPP in THF as a function of pulse energy at a concentration of 6 mM .

5.3.2.6. The Photochemical Stability Measurements from DMAPPP and MDMAPP

The photochemical stability of MDMAPP and DMAPPP in Dimethylformamide (DMF) at a concentration of 6.5 Mm (**Fig 5.24**). The two solutions were excited using the third harmonic of an Nd: YAG (λ=355 nm) with pulse energy of 10 mJ and a repetition rate of 1 HZ. After 3×10^3 pulses, the DMAPPP ASE intensity remained unchanged, whereas, MDMAPP dropped to 15% of its initial intensities after 3×10^3 pulses. Note that the solutions were never circulated or stirred to simulate the condition of a solid-state laser.
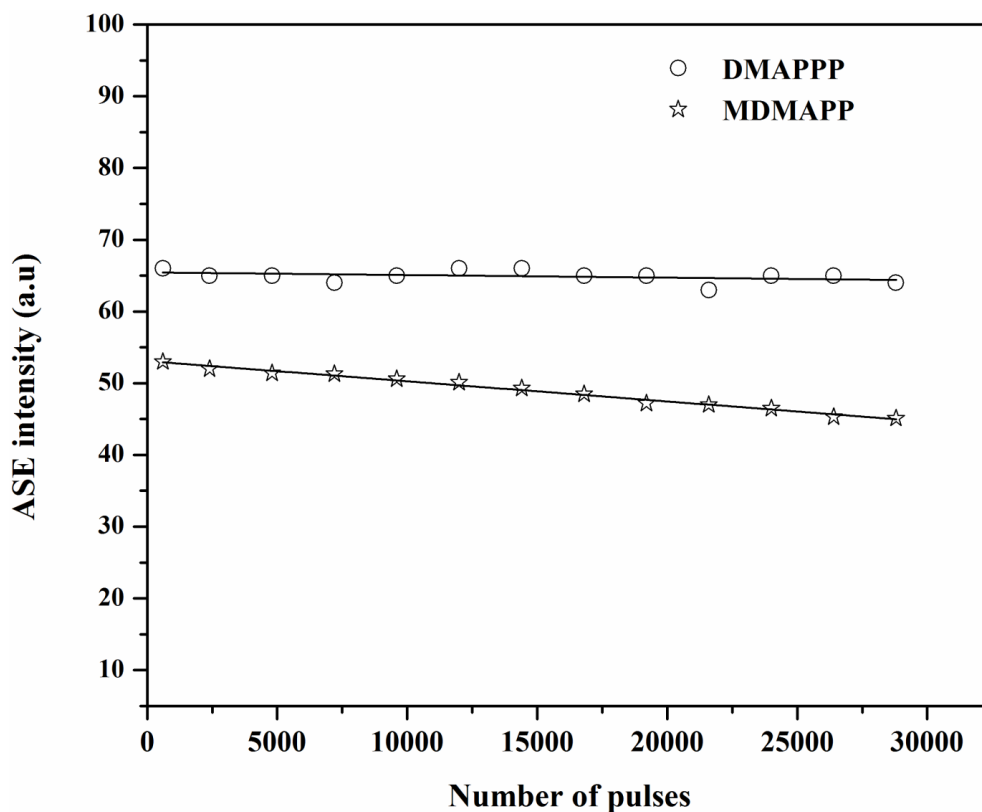
Fig 5.24 The photochemical stability of MDMAPP and DMAPPP in DMF at a concentration of 6mM

5.3.2.7. The Photochemical Stability Measurements from DMAPPP and MDMAPP

(Fig 5.25) shows the photochemical stability of the CPDAPP in DMF at a concentration of 6.5mM was compared to that of DMAPPP in DMF at 6.5mM. These solutions were pumped by the third harmonic (355 nm) of Nd: YAG with pulse energy of 6 mJ and a repetition rate of 1 HZ. After 3×10^3 pulses, the DMAPPP ASE intensity unchanged whereas, CPDAPP dropped to 50% of its initial intensities after 150×10^2 pulses. Note that the solutions were never circulated or stirred to simulate the condition of a solid-state laser.
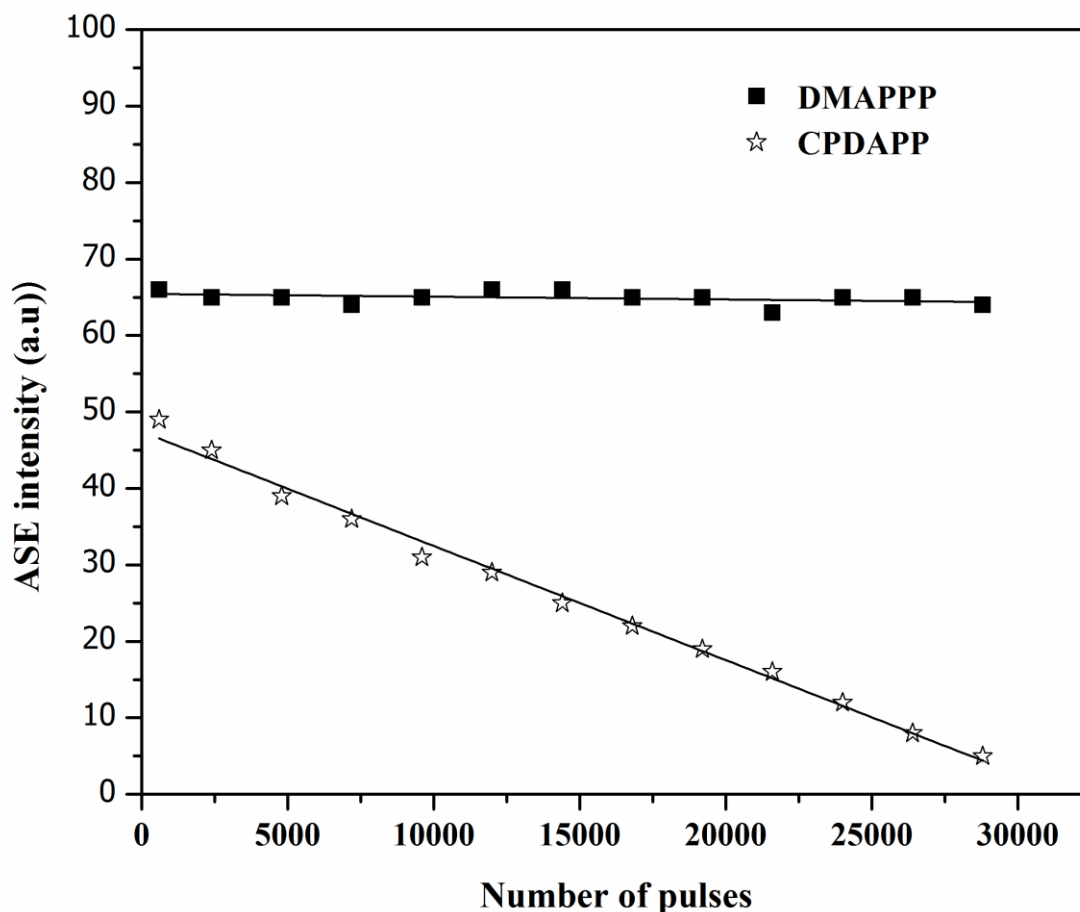
Fig 5.25 The photochemical stability of CPDAPP and DMAPPP in DMF at a concentration of 6mM

CHAPTER VI

6. Conclusions and Recommendations

6.1 Conclusions

In this thesis, we had studied thoroughly the spectral properties of three chalcones laser dyes viz 3-(4-(dimethylamino)phenyl)-1-phenyl-(2E)-propen-1-one (DMAPPP),1-(4-methylphenyl)-3-(4- N, N-dimethyl amino phenyl)-2-propen-1-one (MDMAPP) and 1-(4-chloridephenyl)-3-(4- N, N dimethyl amino phenyl)-2-propen-1-one (CPDAPP). In the beginning, DMAPPP was dissolved in several organic solvents which are: benzene, chlorofrom, tetrahydrofuran, DMF, acetic acid, toluene, acetonitril and acetone at different concentrations. The absorption spectra of DMAPPP in acetone for all studied concentrations showed only one band at 405 nm. That means the DMAPPP does not form in aggregation state (dimer). The absorption spectra of DMAPPP in different organic solvents under same concentration showed only one band with few shift in the band position this due to the solvent polarity.

On the other hand, the fluorescence of DMAPPP in acetone for all studied concentrations showed only one band at 525 nm. That means the DMAPPP does not form in excimer or exciplex state. The fluorescence spectra of DMAPPP in different organic solvents under same concentration showed only one band with few shift in the band position this due to the solvent polarity as mentioned earlier.

The optical properties of DMAPPP were compared with two synthesized chalcone dyes which have closed chemical structure: MDMAPP and CPDAPP. The differences between those three chalcones are (1) DMAPPP is the basic structure without any additional group. (2) MDMAPP has a methyl group in ring **A** position four. (3) CPDAPP has a chlorine group in ring **A** position four (see the chemical structure).

The results showed that when a methyl group was added to ring **A** position four (MDMAPP), there was no change in the peak position of absorption spectra, while a blue shift was observed in the peak position of fluorescence spectra to be at 515 nm. When a chlorine group had been added to the ring **A** in position four, there was a red shift was observed in the in the peak positions of absorption and fluorescence spectra to be at 420 and 535 nm, respectively.

The Stokes' shift and the quantum yield of these chalcones were investigated under different solvents and fixed concentration at 0.65 mM. It could seen that the solvent plays an important role in the variation of the Stokes' shift and the quantum yield of fluorescence values.

The amplified spontaneous emission characteristics (ASE) of DMAPPP were studied in a few organic solutions. From our experiment, the study showed that the variation of ASE intensity depends on many factors such as pump pulse energy, solvent type and concentration.

There is a marked dependence of the relative intensity of ASE peaks on the solvent type. It was found that as the pump pulse energy increases; the ASE intensity of DMAPPP in acetone is slowly increased, while the ASE intensity in tetrahydrofuran increased rapidly, probably because the quantum yield of the DMAPPP in tetrahydrofuran was greater than quantum yield of DMAPPP in acetone.

The study showed also the effects of the concentration on the ASE intensity. It was found that, as the concentration increased the intensity of ASE increased rapidly without saturation.

The ASE of DMAPPP was compared with the MDMAPP and CPDAPP under identical operating conditions. It was found that the ASE of DMAPPP in acetone was higher than MDMAPP and CPDAPP.

The photochemical stability of DMAPPP was also studied and compared with that of MDMAPP and CPDAPP. The results showed that DMAPPP has much better photochemical stability and low pump threshold compared with MDMAPP and CPDAPP.

6.2 Recommendations and Future Work:

Based on the results reported in this thesis, we strongly recommend on the following points:

➢ We recommend more experiments and more studies on these chalcones to verify and support the results which have been obtained.

➢ New experiments on these chalcones using picoseconds laser excitation to study the behavior of the molecules.

➢ Also, new experiments to study the optical properties and the behavior of the molecules of these chalcones as solid state material and thin film.

➢ Intensive efforts for the development of stable solid-state, dye doped laser materials based on chalcones , because the ASE performance of DMAPPP as solutions qualify this compound as a promising candidate for of solid-state laser.

➢ Eventually, new experiments on some other chalcones are potential candidate to produce ASE.

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List of Publications

1. **<u>M. A. Ibrahem</u>**, I. M. Elfaki, A. E. Elfaki. Optical Properties of a Chalcone in Solution. International Journal of Science and pesearch (IJSR) DOI: 10.21275/ART20171601 (IJSR) Volume 6 Issue 3, March 2017 Pages: 12319-7064.

2. **<u>M. A. Ibrahem</u>**, I. M. Elfaki, A. E. Elfaki. Laser Characteristics from a Chalcone in Solution. International Journal of Science and Research (IJSR) DOI: 10.21275/ART20171601 Volume 6 Issue 3, March 2017 *pages: 1324-1326.*

Optical Properties of a Chalcone in Solution

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Abstract: *In this report we had studied the optical properties of chalconein different solvent environments. The results showed that the chalcone has a good photochemical stability and high intense light compared with other dyes. Moreover the absorption and fluorescence spectra were varied from solvent to another under same operational conditions.*

Keywords: Absorption; Fluorescence; chalcone

1. Introduction

The materials, which give color to your clothes and add luster to the face creams are organic compounds, called dyes. When these are dissolved in organic liquids (like, ethanol, chloroform, etc.) the solution becomes highly fluorescent (Recall the fluorescent paints used for warning signals). These dye solution have proved to be excellent media for laser action [1-5].

Laser dyes are large organic molecules with molecular weights of a few hundred. When these organic molecules are dissolved in a suitable solvent such as benzene, methanol, or acetone, can be used as lasing media in a dye laser. Laser dye solutions absorb at shorter wavelengths and emit at longer wavelengths. Many different dyes are nowadays available, and in total they can cover huge wavelength regions like exalite, coumarin, rhodamine, pyrromethene, pyridine, fluorescein, pyridine or crystal can characterize a whole family of dyes with slightly different chemical structures, having somewhat different ranges of emission wavelengths and being distinguished with additional numbers. For example, one may use coumarin 2, 47, 102 or 153 for lasers in the blue to green spectral region [6-8].

Note that many laser dyes and some of the used solvents are poisonous and partly also carcinogenic. One should therefore carefully avoid to expose the skin to such a dye solution, or even to spill the dye by operating a not properly assembled dye circulating system. A particularly hazardous solvent, sometimes used for cyanide dyes, is dimethylsulfoxide (DMSO), which greatly accelerates the diffusion of dyes into the skin [6, 9]

2. Experimental

Chalcone (C6H5CH=CHCOC6H5) was dissolve in a different type of organic solvent, they will produce a different absorption and fluorescence spectra peaks; this is what distinguishes liquid as an active lasing medium compared by gas and solid-state lasing. Third harmonic of Nd: YAG laser, (λ=355nm) with the pulse width7 ns, was used as the excitation source. The UV laser was focused into a quartz cylindrical lens with focal length of 5cm. This was collected by 0.1 mm entrance slit of an EG&G optical multi-channel analyzer (OMA).

3. Results and Discussions

The absorption spectra in the acetone of the chalcone were recorded for a wide range of concentrations from 0.1mM to 1mM. It was found that the shape of the absorption showed a single band at 410 nm and the spectral profile remained the same irrespective of concentration, though the intensity increased with increasing concentration of dye, without any new band as seen in Fig.1. This indicates the absence of any dimer formation. The absorption spectra were recorded of the chalcone for different solvents; the concentration was fixed at 1 mM. It can be seen that when the polarity of the solvent increases the red shit of the absorption increased (see Fig.2).

Similarly the fluorescence spectra of the chalcone were recorded for the same concentrations which mentioned above. It was found that the shape of the fluorescence spectra remained the same irrespective of concentration and there was only one band at 530 nm, though the intensity of the band at 530 nm increased with increasing concentration of dye, without any new band as seen in Fig.3. This indicates the absence of any excimer or exciplex formation.

The fluorescence spectra were recorded of the chalcone for different solvents; the concentration was fixed at 1 mM. It can be seen that when the polarity of the solvent increases the red shit of the fluorescence increased (see Fig.4). Therefore, the solvent plays an important role for the absorption and fluorescence spectra in their positions.

In cases where the polarization interaction is the major contribution factor, Mataga et al[10, 11] have shown that the Stokes shift has a linear variation with the dipole factor, given within square bracketsin the expression

$$\nu_a - \nu_f \, (Stokes'\, shift) \approx \left[\frac{(\varepsilon - 1)}{(\varepsilon + 1)} - \frac{(n^2 - 1)}{(n^2 + 1)} \right] \times Cons\tan t$$

(1)

$$\text{Dipole factor } \Delta f = \left[\frac{(\varepsilon - 1)}{(\varepsilon + 1)} - \frac{(n^2 - 1)}{(n^2 + 1)} \right]$$

(2)

Here, ν_a and ν_f are absorption and fluorescence peaks in wave numbers, ε the dielectric constant and n the refractive

index of the solvents, μ_e and μ_g represent the dipole moment of the solute in the excited state and the ground state respectively, and a is the radius of the solvent cage around the solute.Fig.5 shows a plot of stokes shift as a function of dipole factor for representative solvents. This dipole factor is a measure of dipole-dipole interaction between the solvents and the solute.[11, 12].From Fig.5 early see that the chalcone is more in excited state, the influence of this fact could be seen subsequently.

4. Conclusion

In this paper we had shown the spectral properties of the chalcone dye were investigated in different concentrations and solvents. The results revealed that the polarity of the chalcone is very high according to Mataga plots. Moreover, the solvent polarity makes a significant red shift when the polarity of the solvent increased.

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Figure Captions:

| Fig.1	Absorption spectra of chalcone in acetone for different concentrations.
Fig.2	Absorption spectra of chalcone in acetone for different solvents.
Fig.3	Fluorescence spectra of chalcone in acetone for different concentrations.
Fig.4	Fluorescence spectra of chalcone in acetone for different solvents.
Fig.5	Variation in the Stokes' shift chalcone in solution with a dipole factor for different solvents.
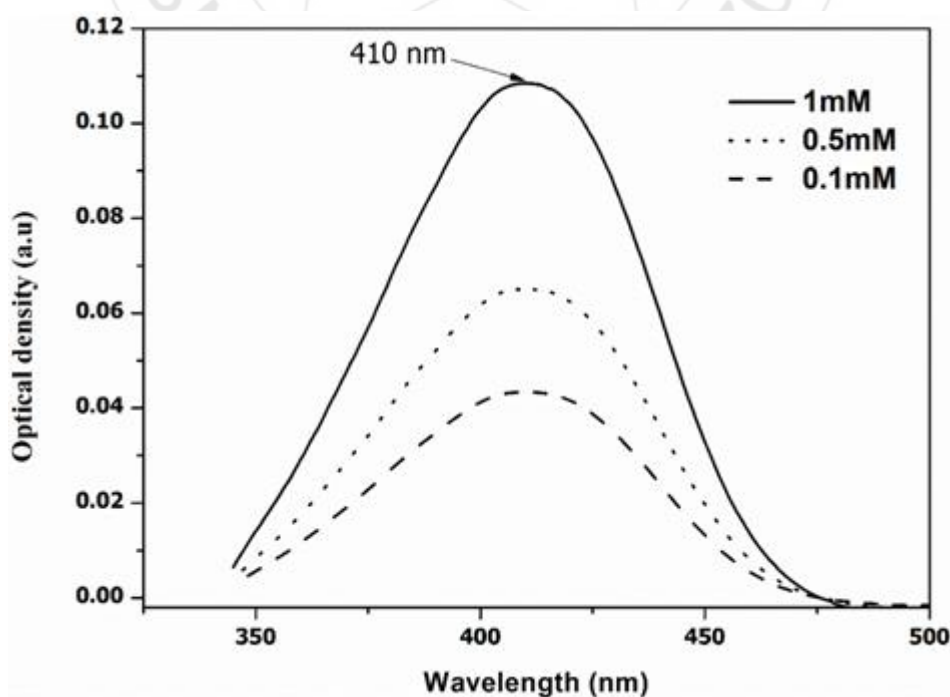
Figure 1
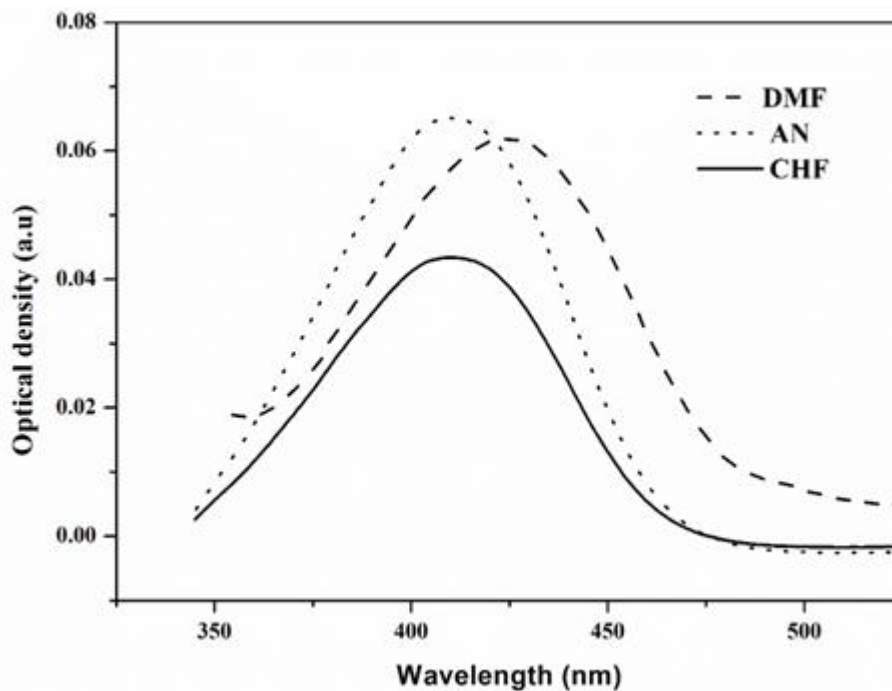
Figure 2

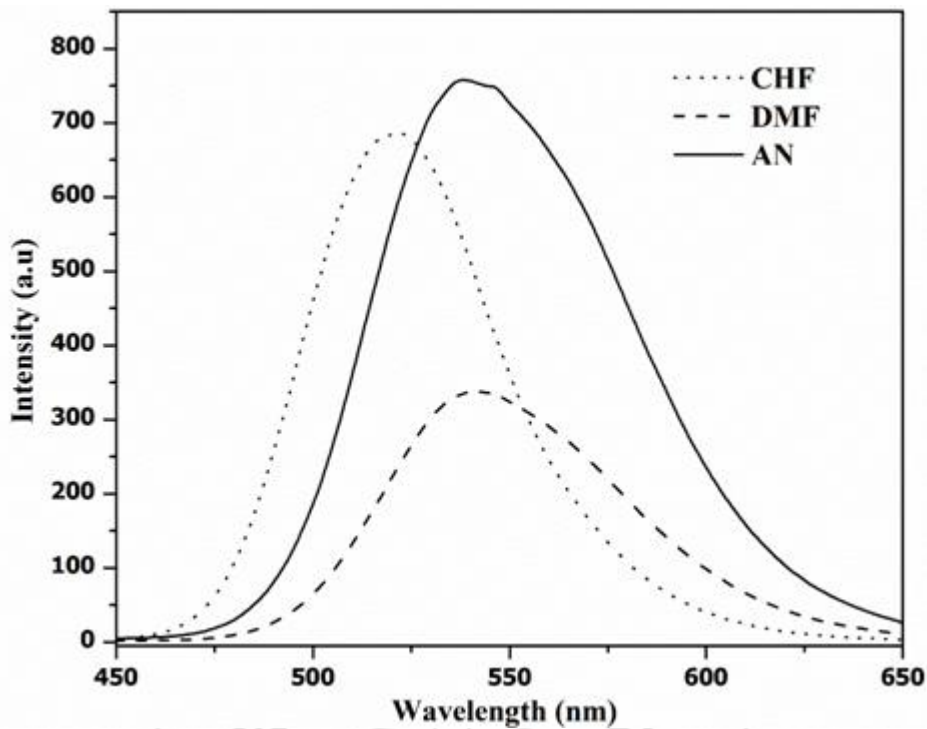
Figure 3
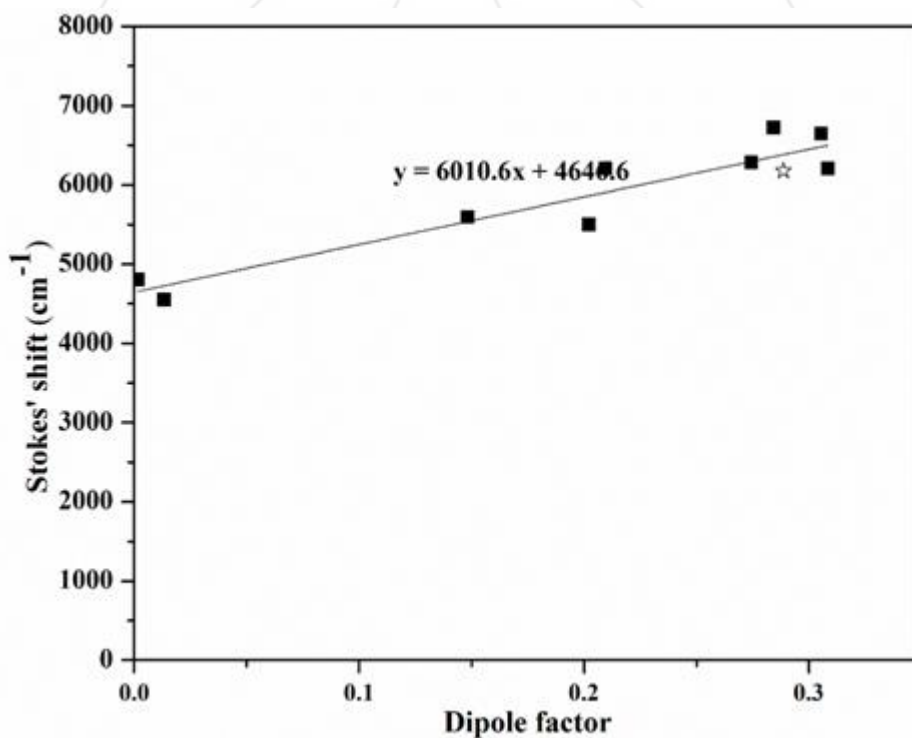
Figure 4

$y = 6010.6x + 4648.6$
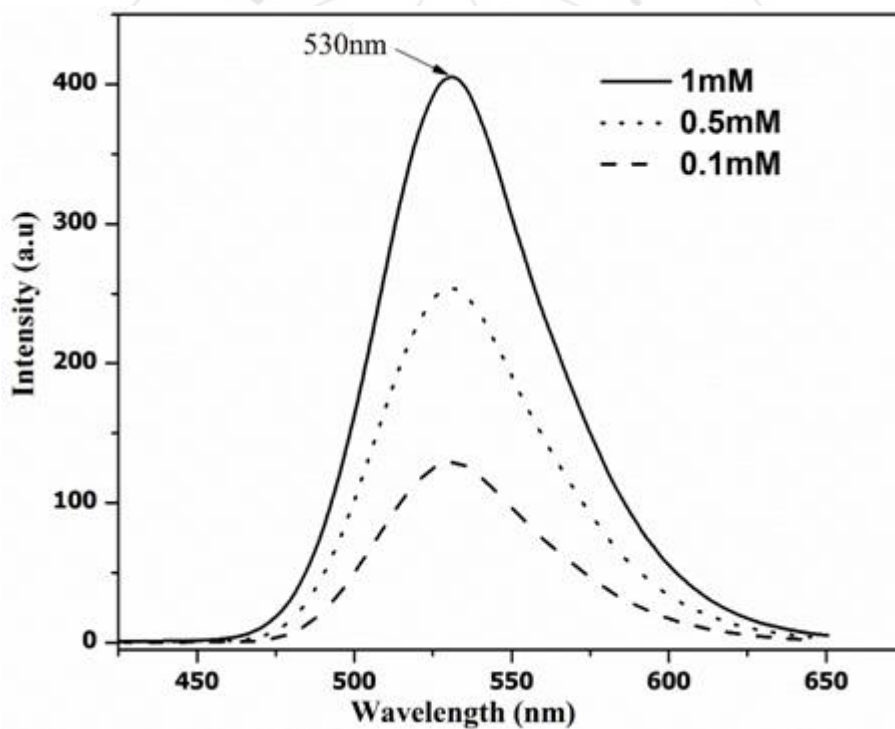
Figure 5

Laser Characteristics from a Chalcone in Solution

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Abstract: *We have studied the laser spectra from conjugated chalcone in a few organic solutions. The laser of the chalcone appears to arise from its monomeric state. Chalcone in solutions of acetone or tetrahydrofuran (THF) was pumped by the third harmonics of an Nd: YAG (355 nm) for different concentrations and pump-pulse energies.*

Keywords: laser, chalcone , solvent effect

1. Introduction

A dye laser is a laser which uses an organicdye as the lasing medium, usually as a liquid solution. Compared to gases and most solid state lasing media, a dye can usually be used for a much wider range of wavelengths. The wide bandwidth makes them particularly suitable for tunable lasers and pulsed lasers. Moreover, the dye can be replaced by another type in order to generate different wavelengths with the same[1].The development of the dye laser has been intimately tied to the systematic search for organic dye structure and dye media in which stimulated emission is observed. An array of photophysical properties such as absorptive, emission (fluorescence) yield, stokes shift, and triplet formation influence the threshold and peak power lasing characteristics. The tailoring of dyes must also be contend with variables having to do with photochemical reactions which degrade dye and produce competitively absorbing product, thus influencing dye service life as other parameters. In the first comprehensive review of laser-dye structures and properties, Drexhage, compiled a table of about three hundred dyes that had been found to laser reasonably[2]. In a later survey covey covering reports on laser dyes through 1980, it has been identified that 546 dyes from various classes of structure work wellwith the advent of powerful laser or flash lamp pump sources and needs for high output and repetition rate, the requirements for photochemical stability of lasing media are extreme. For pulsed lasers, projections as high as 100W power, pulse frequency at 500Hz and 200mJ/pulse have been made[3, 4]. In a review of advances in laser-dye development notes that, the barrier to wider industrial use of the dye laser is due association with dye instability (photo degradation). The service life of a typical rhodamine dye in alcohol on excitation with the unfiltered light of a bank of flash lamps is limited to a few flashes[4].

Laser activity of chalcones
The literature survey has been shown that the laser activity of chalcones is very limited, a crystal of chalcone with two donor auxochromes at para position of ring A and ring B has been studied. It was found that the chalcone is chemically stable and the cutoff wavelength was found to be at 430 nm [5].Sun et al, 2012 have also reported that the compound with such feature has shown a highly fluorescence properties. Theheteroarylchalcones in different solvents has studies and it was showed large red

shift in both absorption and emission spectra in polar solvents, the fluorescence quantum yield is mainly depend on the solvents properties [6].The both of pyrimidine and pyrazole have a lone pair not involved in the π system, this lead to addition electron transfer to that of π system, known as n- π* which also occur at longer wavelength. Pyrimidine is an electron-deficient ring leads to adsorption at shorter wavelengths while pyrazole is a rich one with an opposite properties[7].

The quantum yield to the photoproducts of pyrimidine has been investigated and it was found to be depend on the base auxochromes and phosphate group, phosphate group was shown negative effect, the quantum yield of 0.21 and 0.03 have also reported. The fluorescence of 2-amino-6-hydroxy-4- (3,4-dimethoxyphenyl)-pyrimidine-5-carbonitrile have been studied and shown the quantum yield ranged 0.0073 to 0.0893 [8].

The complexes of pyrimidine bearing β-ketoiminate ligands have also studied and have shown fluorescence quantum yield higher in solid state than in solution. The reported quantum yield were ranged from 0.55- 0.07 [9]. Whereas the fluorescence properties of biaryl pyrimidine nucleosides were shown quantum yield between 0.152 - 0.001 [10]. SamyA.El-Daly et. al (2013) had been measured the photophysical parameters such as absorption, molar absorptive, oscillator strength, dipole moment, fluorescence spectra, and fluorescence quantum yield of 3-(4-dimethylamino-phenyl)-1-(2,5-dimethyl-furan-3-yl)-propenone (DDFP) in different solvents. They showed that DDFP dye exhibited an essentially larger redshift of the emission spectra than the absorption one as solvent polarity increases. This fact indicates that the dipole moment of the DDFP dye is higher in singlet excited state than that in the ground one [11] .M. Gaberet.al (2009) were studied the spectral properties of 3-[40-dimethylaminophenyl]-1-(2-pyridyl) prop-2-en-1-one (DMAPP). Cu (II) complexes of were prepared and characterized by elemental analysis as well as spectral studies (IR and UV–vis), ESR, magnetic susceptibilities and thermal studies. The effect of different alcoholic solvents as well as the temperature on the complex formation is studied. The effect of Cu (II) ion on the emission spectrum of the free chalcone is also assigned. The stoichiometry, stability constant, absorption maximum and molar absorptive of the metal complexes as well as the effect of pH, temperature on complex formation are determined spectra photo metrically.

Adherence to Beer's law and Ringbom optimum concentration ranges are determined[12] .

The spectral and photo physical properties of two chalcones containing electron donating and accepting groups with intermolecular charge transfer characteristics were synthesized and characterized using 1 H NMR, 13C NMR and X-ray crystallography by MehboobaliPannipara et. Al (2015). Both compounds showed very strong solvent polarity dependent changes in their photophysical characteristics, namely, remarkable red shift in the emission spectra with increasing solvent polarity, large change in Stokes shift, significant reduction in the fluorescence quantum yield; indicating that the fluorescence states of these compounds were of intermolecular charge transfer (ICT) character. The solvent effect on the photophysical parameters such as singlet absorption, molar absorptive, oscillator strength, dipole moment, fluorescence spectra, and fluorescence quantum yield of both compounds have been investigated comprehensively for both dyes. Anthony synthesized pyrene-containing chalcone derivatives and studied their optical properties in solution and in solid-state. The molecules showed a zero dipole moment at the ground state in contrast to the excited state that exhibited high polar property. The study also revealed that all the molecules were having emission activities that varied according to the substituents appended on the aryl group connected to the carbonyl function of the chalcone. In particular the methoxy functional group greatly contributed to the enhancement of the emission quantum yield in solid-state as compared to the solution [13]. Novel chloroquinoline based chalcones and their derivatives containing 1,2,3-triazole moiety were synthesized and characterized by spectral data and single crystal X-ray crystallography. Their absorbance and emission spectra were investigated and it was observed that compounds having electron withdrawing or halogen substituents on phenyl ring did not show emission. The ground state and excited state dipole moments of compound were determined using solvate chromic methods. The ground state dipole moment was found to be 1.081 D, while excited state dipole moment was calculated to be in the range of 11.969–3.801 D. Thermal stability was also investigated using thermo gravimetric analysis [14]

2. Results and Discussions

2.1 Amplified Spontaneous Emission (ASE) measurements of MEH-PPV

The ASE spectrum of chalcone in tetrahydrofuran (THF) at 1mM was obtained when this solution was excited by the third harmonic of the Nd: YAG (355 nm) The ASE peak was at 450 nm with a narrow spectral bandwidth 6 nm (FWHM). This peak coincided with the maximum of the fluorescence emission spectrum at this concentration as shown in Fig 1. One can immediately see that laser action was produced from the excimericstate.
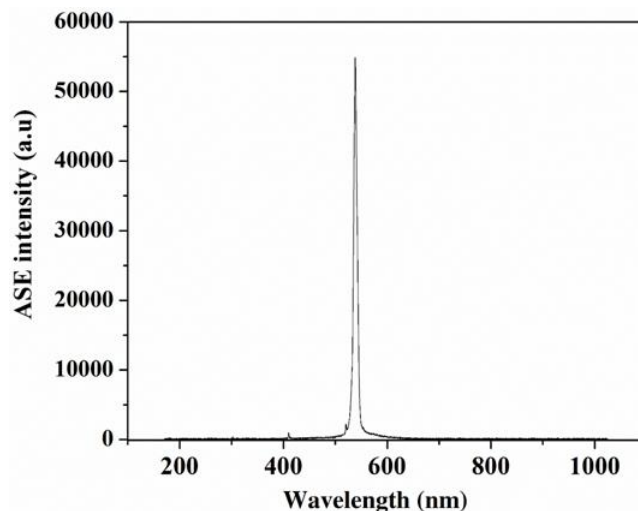

Figure 1: ASE spectrum of chalcone in THF at 1 mM

The variations of ASE intensities of chalcone as a function of pump pulse energy were recorded. The concentration was varied from 0.1 mM with steps of 1 mM the pump power was varied from 6mJ to 12mJ, the solvent in this case was acetone. It is seen in Fig 2 that as the pump power increased, the intensity of the ASE increased linearly for the acetone as shown Fig 2
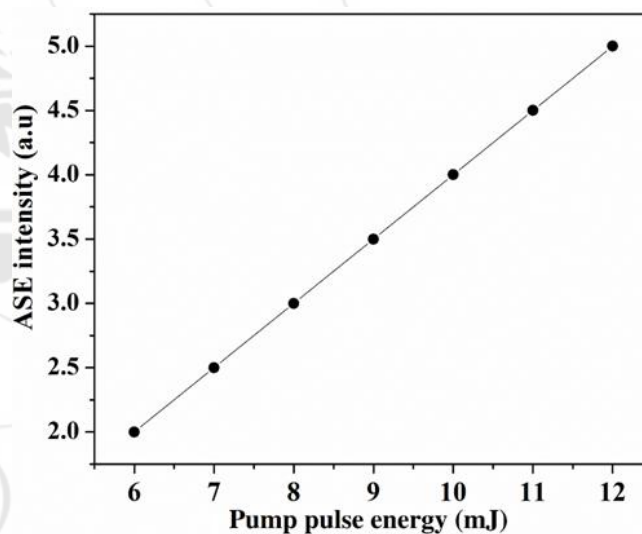

Figure 2: The pump pulse energy dependence of ASE intensity of chalcone in benzene at different concentrations.

Fig 3 shows the ASE intensity of chalcone dissolved in (THF) at different concentrations, where the pump pulse energy being kept at 9mJ. When the concentration increased the intensity of ASE increased until saturation almost sets in at 1 mM .
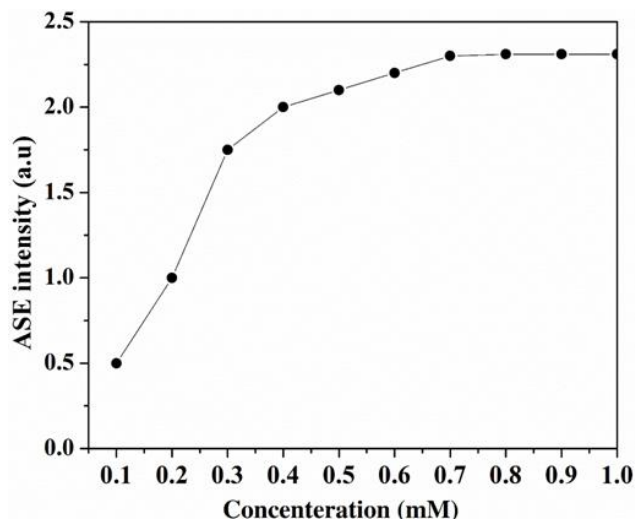
Figure 3: The pump pulse energy dependence of ASE intensity of chalcone in benzene at different concentrations.

3. Conclusion

In conclusion, the excited state dynamic of chalcone molecules was studied in this paper from the measurement of laser spectra. Our results show that the chalcone was capable of to produce high intense laser. This study reveals that these kinds of compounds (amino chalcones) will be promising laser materials in the future.

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