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Utilizing of Rhodamine B dye as a laser active medium

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بسم الله الرحمن الرحيم

قَالُوا سُبْحَانَكَ لَا عِلْمَ لَنَا إِلَّا مَا عَلَّمْتَنَا

إِنَّكَ أَنْتَ العَلِيمُ الحَكِيمُ

صدق الله العلي العظيم

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Dedications

To the paradise of God on earth ... To the owner of a fragrant biography and enlightened thought ... To the one who had the first credit for reaching higher education

my beloved mother.

To my beloved whom I prefer over myself ... To the one who sacrificed for my happiness always and forever

my dear sister "Elaf ".

Shaymaa

Summary

This study included the preparation of cationic form of Rhodamine B (RhB) dye dissolved in methanol solvent with different concentrations of 10^{-3}, 10^{-4} and 10^{-5} M at pH=1. The synthesis has been carried out once by adding hydrochloric acid (HCl) and another one by adding glacial acetic acid (CH_3COOH) to the dye solutions. A sodium hydroxide base (NaOH) and ammonia base (NH_3) were added to the dye solutions for adjustment at pH=10 to generate the zwitterionic form.

The linear optical properties of RhB dye solution before and after addition of acids and bases have been studied by using UV-VIS absorption spectrophotometer. The results showed that the linear optical properties α_o, n_o and k increase with the increase of the concentrations. It was found that the largest values of α_o, n_o and k were 1.59 cm^{-1}, 3.49 and 7.16 which obtained by using hydrochloric acid at the concentration of 10^{-3} M.

The highest values of the real and imaginary dielectric constants were found to be 12.24 and 5.01 respectively for the cationic form generated by adding strong acid to the dye solution at the concentration of 10^{-3} M which has the lowest values of the optical energy gap for the allowed and forbidden indirect transitions at the same concentration.

Fluorescence spectra of RhB dye solution before and after addition were studied by using fluorescence spectrophotometer. It has been established that the quantum efficiency increases with the decreases of the concentration for all solutions. The quantum efficiency value was raised from 0.54 for the pure dye solution at the concentration of 10^{-3} M to the largest value 0.91 for the zwitterionic form generated by adding strong base to the dye solution at the concentration of 10^{-5} M, this indicates that it can be used as an active laser medium. When the strong acid had added to the dye solution, the fluorescence spectra of the dye solution quenched. In

comparison to the strong base, the quantum efficiency of the weak acid and base added to the dye solution increased very little.

The nonlinear optical properties have been investigated by using Z-Scan technique in two cases Open aperture and Close aperture for obtaining nonlinear absorption coefficient (β) and nonlinear refractive index (n_2), respectively. The measurements performed using diode pump solid state laser operating at 457 nm wavelength.

The results showed that increasing in the nonlinear parameters when the concentrations for all solutions increase. It was found that the largest value of the nonlinear absorption coefficient was 0.156×10^{-3} cm/mW for the dye solution with sodium hydroxide at the concentration of 10^{-3} M, and the largest value of the nonlinear refractive index was of the dye solution with hydrochloric acid at the same concentration which equal to 8.46×10^{-11} cm^2/mW.

Z-Scan measurements of two molecular forms of RhB dye solution shows self-defocusing phenomenon and a negative nonlinear refractive index in the close aperture case, and two-photon absorption in the open aperture case, which makes this dye as a good candidate to use in many nonlinear optical applications such as optical limiting.

Contents

List of Symbols

Symbol	***Description***
α_{H+}	hydrogen ion activity
I	Intensity of the incident beam
I_T	Intensities of the transmitted beam
I_R	Intensity of the reflected beam
I_A	Intensity of the absorbed beam
T	Transmittance
R	Refractance
A	Absorbance
h	Planck's constant
υ	Frequency of incident photon
l	Path length of the light through sample
c_A	Concentration of absorbing molecules
ε	Molar extinction coefficient or molar absorptivity of sample
S_0	Ground state
S_1	First excited singlet state
S_2	Second excited singlet state
T_1	First excited triplet state
T_2	Second excited triplet state
q_{fm}	Fluorescence efficiency
K_{fm}	Radiative emission probability
τ_{fm}	Non-radiative life time
τ_f	Fluorescence life time
ΣK_d	Sum of constants for non-radioactive processes for the lowest vibratory state.
τ_{fRB}	Lifetime record of the standard compound (RhB)

Symbol	***Description***
a_{RB}	The area under the RhB fluorescence curve
Φ_F	Quantum yield of fluoridation
α_o	Linear absorption coefficient
t	Thickness of the sample
n	Refraction index
c	Velocity in space
v	Velocity in the medium
n_o	Linear refraction index
λ	Wavelength of the incident beam
E_g	Energy gap
k	Wave vector
r	Exponential constant depended on the transition type
B	constant depended on the material type
E_{ph}	Phonon energy
ε_{real}	Real parts of the dielectric constant
ε_{im}	Imaginary parts of the dielectric constant
E	Applied electric field
P	Polarization
ε_o	Permittivity of free space
χ	Linear susceptibility of the medium
$\chi^{(1)}$	First-order (linear) susceptibility tensor
$\chi^{(2)}$	Second-order nonlinear susceptibility tensor
$P^{(1)}$	First-order polarization
$P^{(2)}$	Second-order polarization
S	Aperture of linear transmittance
β	Nonlinear absorption coefficient

Symbol	***Description***
α	Total absorption coefficient
ΔT	Normalized transmittance difference between peak and the baseline at (Z=0) in the open-aperture Z–Scan
n_2	Nonlinear refractive index
K	Wave number
I_o	Intensity of the laser beam at focus (z = 0)
P_o	Laser input power
ω_o	Beam radius at the focal point
L	True length of the sample
L_{eff}	Effective length of the sample
$\Delta\Phi_o$	The on - axis phase shift of the laser beam traversing the medium
ΔT_{P-v}	The difference between the peak and valley transmittances (T_p and T_v) for the closed-aperture Z–Scan
r_o	Diameter of the slit
I_s	laser saturation intensity
R	Transition rate from the ground state to the excited state
w	Weight of the dye dissolved in methanol solvent
V	Volume of the methanol solvent
C	Concentration of the dye solution
C_1	Primary concentration
C_2	New concentration
V_1	The volume before dilution
V_2	The volume after dilution

List of Abbreviations

Abbreviation	***Full Name***
RhB	Rhodamine B dye
H	Hydrogen
N	Nytrogen
O	Oxygen
S	Sulfur
F	Fluorine
Cl	Chlorine
Br	Bromine
I	Iodine
Ph	potential of hydrogen
ClO^{-4}	Percholate ion
Rh6G	Rhodamine 6G
PMMA	poly methyl methacrylate
NLO	Nonlinear Optics
CA	closed aperture
OA	open aperture
TAP	two-photon absorption
SA	saturable absorption
RSA	Reverse saturable absorption

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Chapter One

Introduction

1.1 Introduction

There are many different types of organic compounds, but all have carbon as their principal constituent atom. These carbon atoms form a carbon skeleton or carbon backbone that has other bonded atoms such as H, N, O, S, and the halogens (F, Cl, Br, and I) [1].

The laser dye very often highly colored substances play the major role in the overall performance of any dye laser. Both pulsed and continuous operation is possible. In addition, their unique photophysical properties make them ideal candidates for the generation of ultrashort light pulses. With mode-locking, pulses shorter than 100 femtoseconds have been obtained. Hyperfine tuning of the output has permitted many exciting experiments in spectroscopy [2]. The first organic compounds to exhibit laser action were organic dyes that also exhibited strong fluorescence. Now all organic compounds that exhibit laser action are called laser dyes [3].

For effective performance, dye molecules should have the following characteristics [4]:

1- Strong absorption at excitation wavelength and minimal absorption at lasing wavelength, i.e., minimum overlap between absorption and emission spectra.

2- High quantum yield (0.5–1.0).

3- Good photochemical stability.

4- A short fluorescence lifetime (5–10) ns.

5- Low absorption in the first excited state at the pumping and lasing wavelengths.

6- Low probability of intersystem crossing to the triplet state.

7- Laser dyes have to be very pure since impurities frequently quench the laser output.

1.2 Organic Laser Dyes

Laser dyes are Hydrocarbons unsaturated compounds where the advantage of its containing to double or triple bonds is conjugated with chains of carbon atoms. This system has the advantage of light absorption in the range of 200-700 nm and the transmission spectrum of absorption in the visible region which makes them as promising species in the applications of dye laser [5].

Organic dyes, usually have strong absorption bands in the ultra-violet or visible range of the spectrum. When excited with light of the appropriate wavelength they display intense, Stokes-shifted broad-band fluorescence spectra. The broad-band structure of absorption and fluorescence is due to the large number of atoms, which contribute to the spectroscopic properties of a dye molecule, leading to electronic levels which are composed of a quasi-continuum of vibrational and rotational sublevels [6].

The Rhodamine dyes are a known series of dyes, e.g., the first member of the series, rhodamine B was synthesized as early as 1887. All of the rhodamines are based structurally on xanthenes, which contain chromophore with amino or hydroxyl groups meta to the oxygen. Rhodamines are commercially the most important amino xanthenes .They cover the wavelength region from 500-700 nm and are generally very efficient [7]. Since Rhodamine B molecules are endowed with emission and absorption properties in the visible range , they may be used as probes in a myriad of applications. The carboxyl group participates in a typical acid–base equilibrium, which the acid and basic forms are strongly colored and luminescent [8]. Its commonly used as an active medium in tunable lasers due to its high fluorescence quantum yield [9].

1.3 Application of Organic Laser Dyes

Organic dyes have various applications in many scientific branches due to their high fluorescence quantum yield and broad gain bandwidth . The wide bandwidth makes them particularly suitable for tunable ultrafast pulse generation [10].

Industrial applications of laser dyes include separation of isotopes of important radioactive elements such as Uranium. Uranium is used as fuel in the nuclear power reactors to generate electricity. The medical applications of dye lasers are some of the most important clinical applications. Medical applications of laser dyes include skin treatments, including tattoo removal, diagnostic measurements, lithotripsy and activation of photosensitive drugs for photodynamic therapy, etc. Laser dyes also uses in the Optical communications, Image processing, Switching, 3D data storage and optical limiting [11].

Rhodamines are important fluorescent dyes with a large variety of technical applications such as its use as an active medium in tunable dye lasers, in light collectors and solar concentrators, and also as quantum counters or reference materials for fluorescence measurements [12].

1.4 Classification of Dyes

Normally, dyes are classified in two separate ways , either accordance to their chemical structure or according to the method of application. Around thirty different groups of dyes can be discerned based on chemical structure. Organic dyes is one of most used in dye laser and classified according to their chemical structure in to [13] :

1. Poly methane dyes: gives a laser action in near IR (0.7-1.5) μm.
2. Xanthene dyes: gives a laser action in visible region (500-700) nm.
3. Coumarine dyes: gives a laser action in blue – green region (400-500) nm.

4. Scientillate dyes: gives a laser action in UV-region (λ< 400 nm).

The approximate working ranges of various laser dyes are shown schematically in figure (1.1)

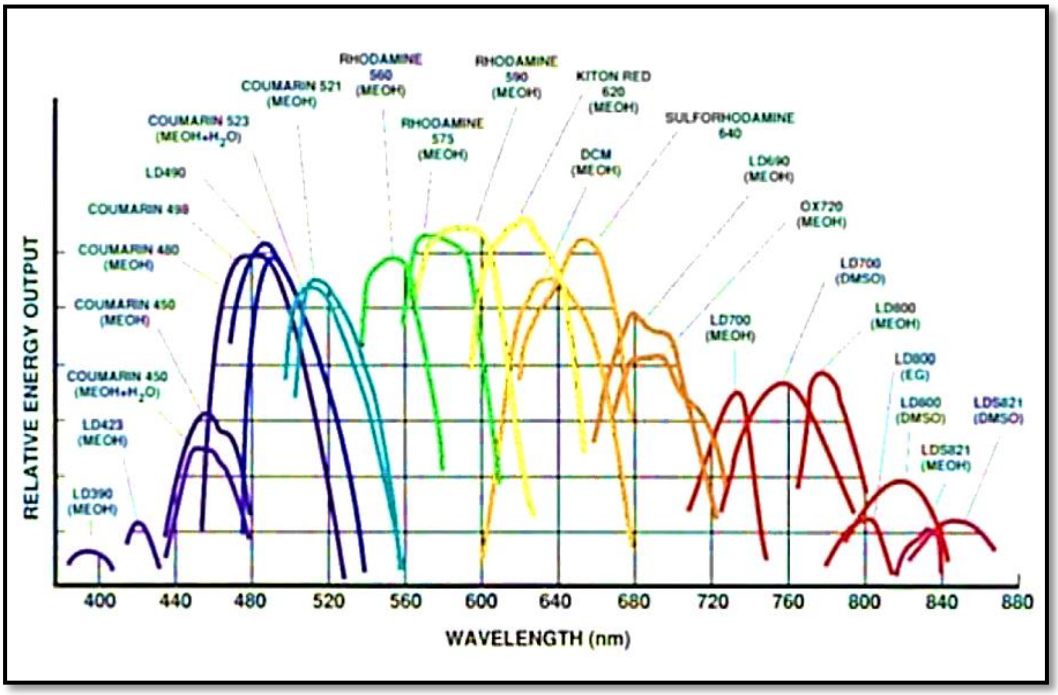


Figure (1.1) : Laser dyes [4].

1.5 Parameters Affecting on Properties of Laser Dye

There are many factors that affect the laser properties of the dyes. The solid laser active medium, the liquid and the gas are generally affected by the design conditions of the laser system. In liquid laser active circles, special factors are affected by the concentration of the solution, the type of solvent, the viscosity of the solution and its acid, and all the influencing factors affect the electronic structure i.e the distribution of the electrons of the effective medium at its energy levels, the molecular electronic energy transitions, molecular oscillatory energy, which changes the wavelength ranges of the emission spectra in the active medium, especially the laser pigments, and this has led to the possibility of synthesis (change wavelength) of the dyes, these include [14].

1.5.1 Concentration effect

The concentration is one of most important parameters that has influence on the organic dyes, where in a very dilute samples, dye dissolves completely into monomers. In such kind of dye solutions the intrinsic absorption of the dye molecules is affected by dye-solvent interaction. Dye-dye interaction is negligible because of the large average distance between the dye molecules in dilute solution. By increasing dye concentration dimer or higher aggregates are formed. Increasing the dye concentration leads to red shifts, that may be caused by changes in the environment of dye molecules, such as changes in polarity or polarizability. This leads to interactions between neighboring molecules, which lowers their excited state energy and produces a red shift in the spectra. At high concentrations the dye-dye interaction gains be importance since the mean distance between dye molecules becomes small and this leads to deviation from the Beer-Lambert law [15].

The molecular association of ionic dyes in solutions due to the strongly attractive electrostatic forces is a well-known phenomenon. The presence of aggregates in the dye solutions may influence considerably in their photophysical behavior. The strength of the molecular association depends on the several factors including the dye concentration. The dye aggregation leads to a strong coupling of the molecular transition dipoles, resulting in excitonic absorption band, which is considerably different from the absorption of the monomeric species. The presence of the aggregates formed by ionic dye molecules can be detected from the observed fluorescence quenching, deviation from the Beer's law in high concentration [16].

In particular, it is assumed that the changes in absorption and fluorescence spectra of diluted and moderately concentrated alcohol solutions in RB are mostly due to the equilibrium shift from zwitterionic to cationic form of the dye, whereas at very high concentrations the changes in RB characteristics result from aggregation. Since all the absorption and fluorescence spectra of both molecular forms overlap strongly [17].

1.5.2 Solvent polarity effect

Solvent polarity is the most significant property which can alter the position of the absorption or emission band of molecules by solvating a solute molecule or any other molecula species introduced into the solvent milieu. On the other hand, the fluorescent dye molecules are complex organic molecules which might carry charge centers and are thus prone to absorption changes in different media [18].

Among the numerous ways of determining excited state dipole moment with electrooptical methods, the solvent-shift method is the simplest and the most widely used. The observation of solvent induced shifts of electronic bands of molecules has been used extensively in order to study the changes in electronic distribution in excited states of solute molecules. The dipole moments of a molecule in the ground state and excited state depend on the electron distribution in these states. A change of solvent is accompanied by a change in polarity, dielectric constant and change in polarizability of the surrounding medium. Thus the change of solvent affects the ground state and the excited state differently [19].

A solvent change which brings about shifts in both absorption and fluorescence wavelengths indicates that the solvent interacts with the solute in the ground state while that which alters the fluorescence wavelength alone indicates that the solvent interacts with the solute in the excited state [20].

The solvent shifts can be accounted in terms of the overall effect of the interaction forces (which are mainly of van der Waals type) on the π-electron system of the molecule. It is also known that as the electron system becomes less localized, the transition energy becomes smaller resulting in a bathchromic shift (red shift) and its opposite effect gives rise to a hypsochromic shift (blue shift) [19].

Rhodarnine B is an important laser dye. With unesterified phenyl carboxylic group at the 9-position, it shows great sensitivity to the solvent environment because of the possibility of a number of molecular forms such as two ionic forms, zwitterionic ($RB^{\pm}$) and cationic (RBH^{+}) in protic solvents [21]. Protic solvents such as methanol stabilize the zwitterion. A steady decrease in the intensity of the visible absorption of RB is observed with progressively longer aliphatic chain length of the alcohol [22].

1.5.3 Effect of pH on molecular structure of dye laser

The concept of pH is one of the most fundamental in chemistry, but has a broad significance in many other disciplines such as biochemistry, biology, physics [23]. The pH of a substance is a measure of its acidity. Because acids donate hydrogen ions, when they are added to a solution they increase its hydrogen ion concentration. The addition of a base decreases the hydrogen ion concentration in a substance because bases accept hydrogen ions [24].

The pH is notionally defined for any medium as the decimal logarithm of the reciprocal of the hydrogen ion activity ($\mathrm{pH} = -\log_{10}\alpha_{\mathrm{H}^{+}}$) in that medium. A value of (pH=7) defines a ‘neutral’ medium where the proton and its hydroxyl counterion are present in equal concentrations. Media with (pH<7) are characterized as acidic, whereas those with (pH >7) as alkaline [25].

Rhodamine B exists in solution as three different forms which depend on the solution pH. At low pH (-1 to 0) form colorless Lacton is favored, but in a solution of moderate, an intensely colored the cation can be assumed. In a solution of higher pH the highly colored zwitterion will be the favored form. The following figure shows Molecular forms of RhB [22,26].

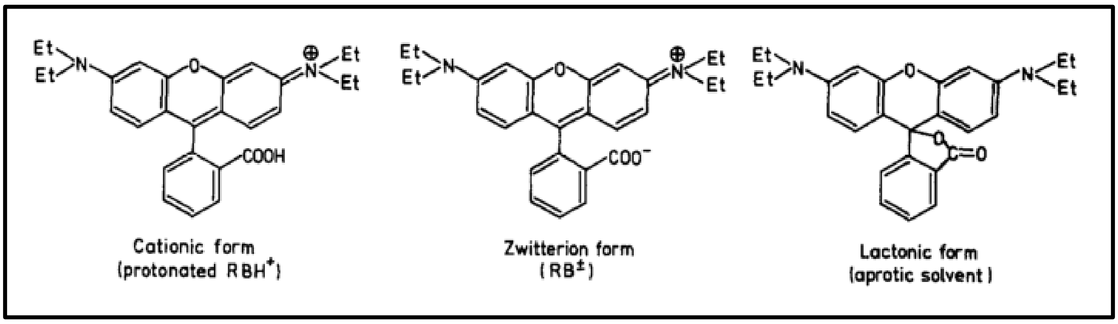


Figure (1.2): Molecular forms of RhB [21].

pH of the solvent is important. Many organic dyes may behave as weak acids or bases. In proton solvents therefore partial or complete dissociation or protonation can occur in the ground state species of the solute. In effect new species having their own unique absorption and emission spectra are formed. It is also known that the acid-base properties of the excited states, are often different from those of the ground state. A dye may become a stronger acid or a stronger base in the excited state. This property results in dissociation, protonation reactions in the excited state only. The reaction products are unstable in the ground state with the result that they manifest themselves by changing the fluorescence spectrum only leaving the absorption spectrum unchanged [13].

1.5.4 Charge transfer effect

It is known that fluorescence of dyes is quenches by specific negative ions, and the quenches efficiency depends on the chemical nature of the negative ion, so we find it very strong in the case of the iodine ion (I^-), and it decreases in the following order:, bromine ion (Br^-) and chlorine ion (Cl) and Percholate ion (ClO^{-4}). Most chromoform of laser dyes carry a positive charge, so these dyes usually have a negative ion such as the chlorine ion

(Cl^-) or the iodine ion (I^-). The fluorescence efficiency is affected by the ion accompanying of the chromophore and depends on the concentration and the polarity of the solvent. As we note that the fluorescence efficiency of (R6G iodide) and (R6G Perchlorate) solutions with molar concentration (10^{-4}) M in ethanol solutions are similar and very high, and this indicates that there is no quenches of negative ions in this case. fluorescence of (R6G iodide) solution at the same concentration in a non-polar solvent as chloroform is almost completely quenched [27].

It has been found that the dye salts completely dissociation in a polar solvent such as ethanol, but in reality these salts do not dissociation in chloroform. For this reason, the negative ions in ethanol do not have enough time to reach the molecules of the excited dye during their lifetime, while in chloroform the negative ions are directly present for interacting with the molecules of the excited dye. As mentioned Matsunage and his group that rhodamine-type dyes, i.e., (Rh6G) and (RhB) were formed as salts with (Cl). This (Cl) quenches the excited-state dye molecules by a charge transfer interaction. when weak acid was added to the (Rh6G) solution the laser intensity increased. There may be a substitution from (Cl) of dye molecule to the weak acid, which sets the dye molecule free of quenching due to the charge transfer, But for (RhB) the increase in the laser output might instead be due to the interrupted aggregation caused by the addition of (KOH) and (NaOH) [28].

1.6 Acids and Bases

Acids and bases are common substances. There are three major theories of substances known as acids or bases. The Arrhenius definition states that an acid produces (H) in solution and a base produces (OH). This theory was developed by Svante Arrhenius in (1883). Later, two more sophisticated and general theories were proposed. These are the Bronsted-Lowry and the Lewis definitions of acids and bases [24, 29].

The Arrhenius Definition is based on the autoionization of water and is limited because it can only describe acids and bases in aqueous environments. Arrhenius defined an acid to be a compound that dissolves in water to make hydrogen ions and a base as a compound that dissolves in water to yield hydroxide anions, Bronsted-Lowry defined an acid and base reaction as one that involves a hydrogen ion transfer between two reactants. The acid is the hydrogen ion donor (Bronsted acid) and the base is the hydrogen ion acceptor (Bronsted base). Lewis defined acid as any substance that accepted an electron pair. A base, on the other hand, is any substance that donates an electron pair [30,31].

Acids and Bases classifications based on their ionization in water into [24]:

1.6.1 Strong and weak acids

Acids are classified as either strong or weak, based on their ionization in water. A strong acid is an acid which is completely ionized in an aqueous solution. A weak acid is an acid that ionizes only slightly in an aqueous solution. Acetic acid is a very common weak acid. Any acid that dissociates 100% into ions is called a strong acid, HCl is an example of a strong acid. If it does not dissociate 100%, it is a weak acid, CH_3COOH is an example of a weak acid.

1.6.2 Strong and weak bases

A strong base is a base that is 100% ionized in solution such as NaOH. If it is less than 100% ionized in solution, it is a weak base. All strong bases are OH compounds. So a base based on some other mechanism, such as NH_3 which does not contain OH ions as part of its formula, will be a weak base.

1.7 Literature Survey

Several researches on study Linear and nonlinear properties in organic dyes.

C. Liu ***et al.*** [32] synthesized a novel rhodamine-B cation fulleride salt by metathetical reaction. Its tetrahydrofuran solution was prepared and the fluence-dependent transmission was measured with 10-ns 532-nm laser pulses in a collimated optical setup.The results suggested that the optical limiting response of RhB cation fulleride salt is mainly a result of reverse saturable absorption induced by fullerides. A. A. Abd Al.Fhdawi [28] studied photophysical properties (absorption, luminescence quantum yield and radiative lifetime) of RhB dye inclusion different concentrations (10^{-4}-10^{-6}) M and in different solvents such as chloroform, methanol and dimethyl sulfoxide. The results indicated that the intensity and wavelength of absorption and Luminescence spectra maxima depended on increasing or decreasing the dye concentration. N. A.A. Al.Temeeme ***et al.*** [33] studied Absorption, flourescence, quantum yield and lifetime of RhB in methanol at a concentration of (10^{-4} -10^{-6}) M. The results had been pointed out there are shifts to the low energy (long wave length) as the concentration increases, while the quantum yield decreases and lifetime increases. The shift in spectra is toward long wave lengths as the concentration increases. These changes have been interpreted in two different ways. On the one hand they are considered as due to dimerization process. On the other, they are attributed to the change of RhB from its neutral form to the cationic one, this theory is based on the decreasing of pH produced when dye concentration increases. R. A. Ali ***et al.*** [34] studied the spectroscopic characteristics of laser dye RhB in ethanol and methanol solvent at concentration of (10^{-4}) M, depending on solvent polarity. The results had been indicated that the increase in the polarity of the solvent occurs displacement in spectra towards the longer wavelengths, and also variation in quantum efficiency value as a function of increasing in solvent polarity and smallness area under the curve as in methanol where is the methanol polarity is larger than ethanol polarity. N. A. A. Al.Tememee ***et al.*** [35] investigated the effects of solvents of various polarities on the electronic absorption and fluorescence spectra of RhB and Rh6G at different concentrations (10^{-4}-10^{-6}) M. The results suggested that the singlet-state excited dipole moments and ground state dipole moments using the variation of Stokes shift along with the solvent's dielectric constant (ε) and refractive indexes (n). The observed singlet-state excited dipole moments were found to be larger than the ground-state ones. Moreover, the obtained fluorescence quantum yield values were influenced by the environment of the fluorescing molecule. Consequently, the concentration of the dye solution, excited singlet state absorption and aggregate of dye molecules has been found to effect the values of the fluorescence quantum yield.

In (2014) A. H. Al.Hamdani ***et al.*** [36] investigated the spectral properties (absorption and fluorescence) of Rhodamine B dye had been studied which was dissolved in chloroform with different concentrations (3×10^{-5}, 8×10^{-5},8×10^{-4}, 5×10^{-4}, 2×10^{-4} and 2×10^{-3}) M at room temperature. The variation in the solvent concentration lead to blue shift in the absorption spectra and red shift in the fluorescence spectra as the concentration increased. It had been noticed that the quantum efficiency decreased as a function of concentration. F. Mata [37] investigated the linear and nonlinear optical absorption behavior of the organic dye, Rhodamine B in aqueous solution for various dye concentrations. The samples exhibited increase in absorption spectrum intensity with increasing concentration, and this agree with Beer-Lambert law. The absorptive nonlinearity for Rhodamine B dye in aqueous solution was investigated under low power continuous wave (CW) laser light illumination at (442) nm, performed using the Z-Scan technique is presented. The samples exhibited reverse saturable absorption. S. A. Razzak ***et al.*** [38] calculated linear optical properties of RhB dye with four concentrations (10^{-3}-10^{-6}) M using the ethanol solvent. the results exhibited decrease in linear absorption coefficient and refractive index, also an increase in the quantum yield and a decrease in the fluorescence level lifetime with reduced concentration. R. S. Alnayli ***et al.*** [5] calculated the optical linear properties by employ UV-visible Spectrophotometer to find the linear index of refraction, the linear coefficient of absorption and the coefficient of extinction for Rhodamine B dye in water solvent at room temperature at different concentrations (10^{-2},10^{-3} and 10^{-4}), the results showed an increase in the coefficient of extinction and index of refraction values with the increase in the concentrations. The properties of nonlinear optical of the samples for example non-linear index of refraction, and non-linear coefficient of absorbance were measured by using Z-Scan technique performed with diode laser of a continuous wave (CW) with 650 nm wavelength. The result showed that the samples exhibit negative refractive index ($-n_2$) self-defocusing for all concentrations and two-photon absorption for open aperture z-scan so that the laser dye can be applied in nonlinear optics application and it is useful in the optical limiter applications. H. H. Al.aaraji ***et al.*** [39] calculated the fluorescence lifetime and quantum yield of RhB dye in water different concentration (10^{-3}-10^{-7}) M. Results of the calculations showed the highest value of quantum yield at 96% was reached at a concentration (10^{-7}) M while the lifetime decreases. A high quantum yield of this dye allow numerous applications such as optoelectronics applications. W. E. Passos ***et al.*** [40] used UV-Visible absorption and fluorescence to determine the water content in ethanol by using RhB as an optical probe. The results showed that water molecules perform well oriented dipole-dipole interactions (hydrogen bonding) with chromophores groups of RhB, affecting its absorption and emission characteristics. This results point out that common optical techniques can be used to develop a simple, rapid, and precise approach to monitor water in ethanol as far as RhB be used as a probe. F. Mokhtari and N. Tahmasebi [41] investigated the W-doped BiOCl nanoplates synthesized hydrothermally for photocatalytic RhB degradation under visible light. The result show that absorptivity edge shifted towards higher wavelengths as light absorption increased in absence of W under UV and visible light irradiation, because of decrease in gap of band (E_g) and rise in absorption of light produced by development of E_g in BiOCl's forbidden energy gap. R. Abadhe ***et al.*** [42] investigated the optical properties of TiO_2 and CdS nanocomposites, Under natural light irradiation, they were used for photocatalytically reduce RhB. In natural light radiation, these nanocomposites were employed to photocatalytically degrade RhB. It was discovered CdS and TiO_2 has the highest degradation efficiency of 98.74 percent inside 60 minutes when linked to TiO_2 NPs, which has a degradation efficiency of only 66.40 percent. Electrochemical and photoluminescence studies were used to investigate the increased photocatalytic efficacy of bare NPs and CT nanocomposites due to charge transfer capabilities. S. A. Raza ***et al.*** [43] studied the interaction between RhB and varying concentrations of graphene with spectroscopic techniques. Absorbance measurements indicated the formation of an RhB–graphene complex and a significant decrease in RhB absorbance due to complex formation. Fluorescence quenching studies revealed that graphene is a good quencher of RhB emission and that the RhB-graphene complex is non-emissive in nature, leading to an apparent quenching efficiency of 49%. A good fluorescence quenching had been suggested that RhB and graphene could be a promising donor–acceptor pair for emerging photovoltaics.

1.8 Aims of the Work

The main aims of this work are:

1. Preparation two form of the RhB dye by adding acids and bases using pH meter.
2. Investigation of linear and nonlinear optical properties of pure RhB dye in methanol solvent at different concentrations.
3. Study the effect of adding acids and bases on the performance of the RhB dye.
4. Using RhB dye with strong base as a possible active laser media.

Chapter Two

Theoretical Part

2.1 Introduction

This chapter covers a general description of the theoretical parts measurements; linear and non-linear optical properties of RhB dye solution. Finally, this chapter gives a theoretical review including all the relations, scientific explanations, and the equations which are used in this thesis.

2.2 Interaction of Light with Matter

The interaction between the nature and distribution of charges within the material (electronic, molecular, ionic) and electromagnetic radiation falling on the material results in the appearance of the optical properties of the material. A number of processes can occur when an electromagnetic beam falls on the material and their interaction together as part of the light radiation turns to heat by absorbing it by the material. The other part is called the transmitted radiation as the input passes through the material without losing energy. While the remaining portion of the light radiation is reflected from the surface of the material [44].

The intensity (I) of the beam incident to the surface of the solid medium must equal the sum of the intensities of the transmitted (I_T), absorbed (I_A), and reflected beams (I_R), denoted as the following equation [45]:

$$I = I_T + I_R + I_A \qquad (2\text{-}1)$$

The alternate form of above equation is:

$$T + R + A + S = 1 \qquad (2\text{-}2)$$

Where (T) is the transmittance, (R) is refractance, (A) is Absorbance.

2.3 Photophysical Processes

The photophysical processes which occur in the aromatic hydrocarbons is defined as a physical process resulting from the electronic excitation of a molecule or system of molecules by non-ionizing electromagnetic radiation [46].

For any particular molecule, several electronic states exist. There is a combination of different available orbits (singlet states S_o, S_1, S_2,) and spin orientations (triplet states T_1, T_2), that are further divided into a number of vibrational and rotational energy levels. Excitation (e.g., S_o–S_1, S_2) involves the absorption of sufficient energy to raise a molecule's electrons to electronic states of S_1 or S_2. This molecule does not remain excited continually. the ground state S_o is the only stable state, with all other states decaying back to this state. According to the conversation of energy principle, the amount of energy absorbed must be released. This happens via emissions of photons with energy equal to the energy level difference, as well as energy transfer via quantized vibrational exchange (phonons) in the material, and other complex energy transfer mechanisms [47]. A useful approach to understand the details of the excitation and emission process is to render the process in the form of a diagram first conceived by Alexander Jablonski in the 1930, which displaying the energy states of a molecule in the part (a) of below figure, The spectral characteristics related to absorption and emission of energy by a molecule in the part (b) and the times that the various steps in fluorescence excitation and emission and phosphorescence in the part (c) [48].

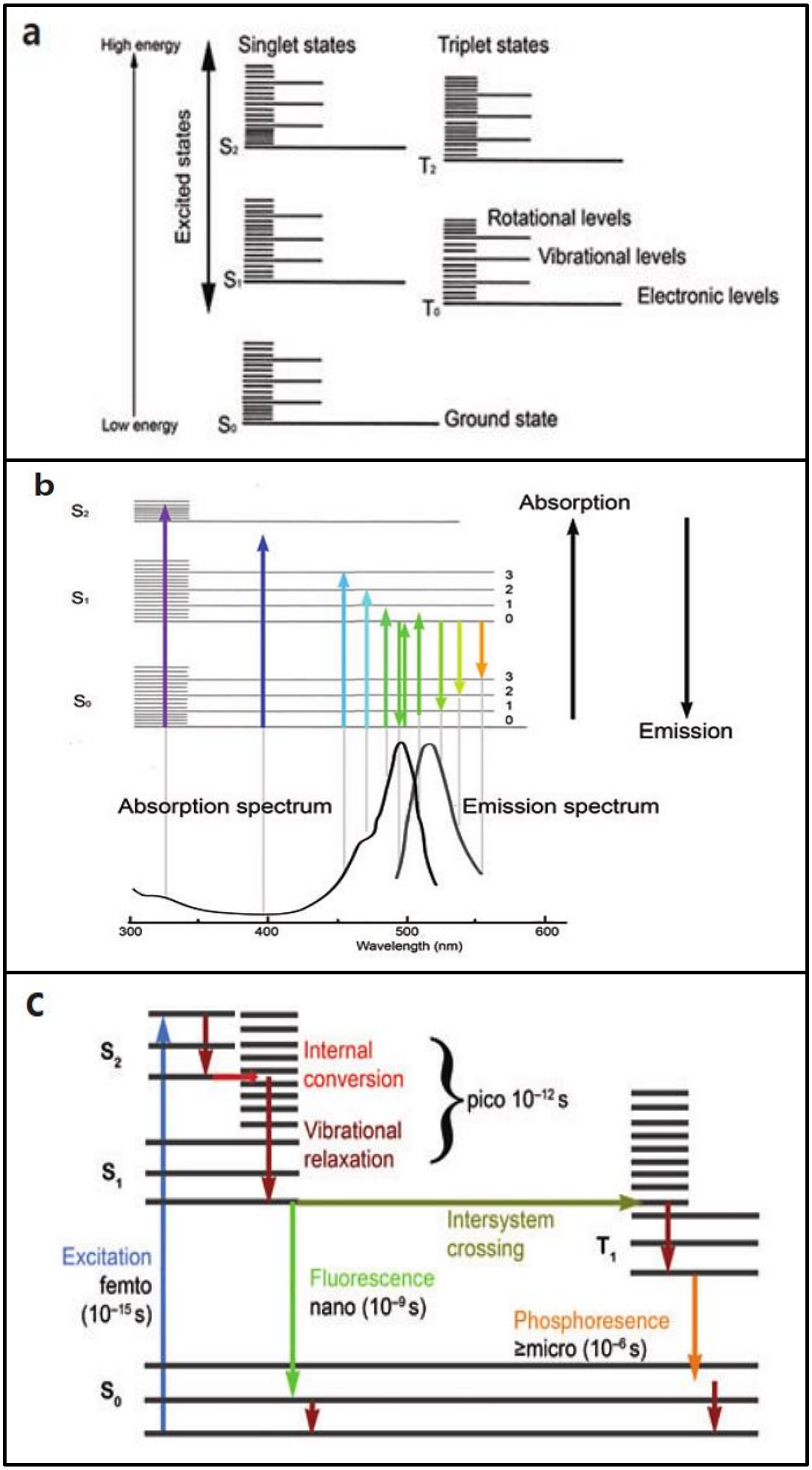


Figure (2.1): Jablonski diagram of fluorescence fundamentals [48] .

2.3.1 Absorbance spectrum

If the electromagnetic radiation falls on the molecule, the force resulting from the interaction of electric dipole moment of the molecule with the electric field of the electromagnetic radiation will lead to irritation the molecule from ground state to excited state. The energy of molecule is equal to the difference in energy between two states [49].

$$\Delta E = h\upsilon \qquad (2\text{-}3)$$

Where (h) is Planck's constant, (υ) is frequency of incident photon.

The optical density or absorbance of a material is a logarithmic intensity ratio of the light falling upon the material to the light transmitted through the material. The absorbance is proportional to the concentration and the thickness according the Beer-Lambert law [50]:

$$A = \log \frac{I}{I_T} = \varepsilon c_A l \qquad (2\text{-}4)$$

Where (c_A) is the concentration of absorbing molecules, (l) is the path length of light through the sample and (ε) is called the molar extinction coefficient or molar absorptivity of the sample. The percentage (I_T/I) is called transmittance. Absorbance is dependent on the wavelength and is often measured as a function of the radiation wavelength, which is called the absorption spectrum. The absorption spectrum is a very important quantitative measure to evaluate optical properties of solutions, it provides several types of information such as the concentration of a solute [50].

2.3.2 Emission spectrum

A stimulated electron cannot remain in an excited state indefinitely; after a short time, it falls or decays back into its ground state, or unexcited level, with a reemission of electromagnetic radiation, there must be a conservation of energy for absorption and emission electron transitions. Several decay paths are the following [51].

2.3.2.1 Radiative processes

Luminescence refers to the emission of light from an excited electronic state of a molecular species. A molecule absorbs light decays to a lower energy excited electronic state, and then emits light, as it radiatively decays to its ground electronic state. Luminescence can be either fluorescence or phosphorescence, depending on the average lifetime of the excited state which is much longer for phosphorescence than fluorescence [52].

2.3.2.1.1 Fluorescence

It is a phenomenon in which a material absorbs light of one color (wavelength) and emits it at a different color (wavelength) [53].

When these molecules absorb a quantum of light, a valence electron is boosted up into a higher energy orbit, creating an excited state S_1. When this electron returns to its original S_o , lower energy orbit (the ground state level), a quantum of light may be emitted. Fluorescence is thus a relaxation process which leads to the loss of some energy prior to the emission of light. The loss of energy through vibrational relaxation means that less energy is available for emission as fluorescence. Because wavelength varies inversely to radiative energy, fluorescence emission is at a longer wavelength (i.e., lower energy) than the light used to excite it [54]. The lifetime (τ) of a fluorophore is the average time between its excitation and return to the ground state [55]. The energy difference between the two states results in the energy of the incident photons being shifted away from the excitation wavelength. If the final energy state of the molecule is higher than the initial state, then the emitted photon will be shifted to a lower frequency, which is designated as Stokes shift. If the final energy state is lower than the initial state, then the emitted photon will be shifted to a higher frequency, and this is designated as an anti-Stokes shift as shown in below figure [56].

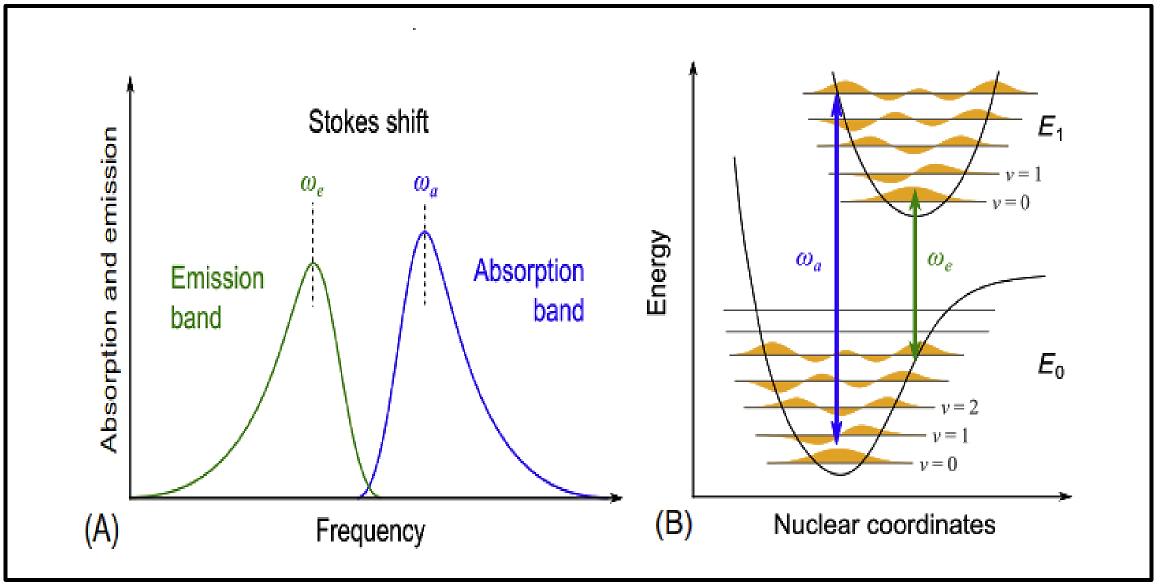


Figure (2.2): Schematic representation of the optical properties of fluorescent dyes and representation of the underlying physical processes. (A) Emission (left) and absorption (right) spectra of a simple fluorescent dye with mirror-inverted bands separated by the Stokes shift. (B) Representation of the electronic energy levels in a fluorescent molecule [57].

2.3.2.1.2 Phosphorescence

Phosphorescence is emission of light from triplet-excited states, in which the electron in the excited orbital has the same spin orientation as the ground-state electron. Transitions to the ground state are spin-forbidden, and the emission rates are relatively slow, these photons are generally shifted to longer wavelengths (lower energy) relative to fluorescence [58].

2.3.2.2 Nonradiative processes

nonradiative processes occur when molecules transition between vibrational levels of different electronic states. Such transitions are normally preceded by radiation less thermal activation of the initial electronic state and followed by radiation less de-activation of the final electronic state [59].

2.3.2.2.1 Internal Conversion

Internal conversion is a non-radiative transition between two electronic states of the same spin multiplicity. In solution, this process is followed by a vibrational relaxation towards the lowest vibrational level of the final electronic state. The excess vibrational energy can be indeed transferred to the solvent during collisions of the excited molecule with the surrounding solvent molecules. When a molecule is excited to an energy level higher than the lowest vibrational level of the first electronic state, vibrational relaxation (and internal conversion if the singlet excited state is higher than S_1) leads the excited molecule towards the 0 vibrational level of the S_1 singlet state. From S_1, internal conversion to S_o is possible but is less efficient than conversion from S_2 to S_1, because of the much larger energy gap between S_1 and S_o. Therefore, internal conversion from S_1 to S_o can compete with emission of photons (fluorescence) and intersystem crossing to the triplet state from which emission of photons (phosphorescence) can possibly be observed [60,61].

2.3.2.2.2 Vibrational relaxation

After a process internal conversion, the molecule relaxes to the ground vibrational level of the first excited singlet state within a few picoseconds, an effect known as vibrational relaxation. As the time required for internal conversion is typically much less than that for fluorescence emission, the following transition occurs from the lowest vibrational sublevel of the lowest excited state. The primary mechanism of relaxation of excited non-emitting molecules is radiation less decay, in which the excess energy is transferred into the vibration, rotation, and translation of the surrounding molecules. The excitation energy is thus dissipated as heat, and the molecule returns to the ground electronic state [62].

2.3.2.2.3 Intersystem crossing

Intersystem crossing in molecules is a non-radiative process involving electron transition between two electronic states with different spin multiplicities. Intersystem crossing may be fast enough to compete with other pathways of de-excitation from S_1 (fluorescence and internal conversion S_1-S_o) [63].

2.4 Fluorescence Quantum Efficiency

The fluorescence efficiency (Φ_{fm}), also known as the quantum yield, indicates the fraction of pump photons that are converted to fluorescence photons per dye molecule, where the maximum value is unity. The quantum yield of fluorescence is a measure of the rate of non-radiative transitions that compete with the emission of light. The knowledge of fluorescence quantum efficiency of organic dyes and its concentration dependence are essential for selecting efficient laser media. In order to evaluate absolute quantum efficiency, we have to consider both the radiative and non-radiative processes taking place in the medium, therefore [64]:

$$q_{fm} = \frac{K_{fm}}{K_{fm}+\Sigma K_d} = \frac{K_{fm}}{K_{fm}+K_{IC}+K_{ISC}} \qquad (2\text{-}5)$$

$$K_{fm} = \frac{1}{\tau_{fm}} \qquad (2\text{-}6)$$

$$\tau_f = \frac{1}{K_{fm}} + \frac{1}{\Sigma K_d} \qquad (2\text{-}7)$$

Where (K_{fm}) is radiative emission probability, (τ_{fm}) is radiative life time, (τ_f) is fluorescence life time, (ΣK_d) is the sum of constants (rate constants) for non-radioactive processes for the lowest vibratory state.

The life time of fluoridation (τ_f), record compound known to his life time, as well as the area under the curve, as in the following relationship equation which is adopted in calculations in this research [66]:

$$\tau_F = \frac{a \times \tau_{fRB}}{a_{RB}} \qquad (2\text{-}8)$$

Where (τ_{fRB}) represents the lifetime record of the standard compound (3,230 ns) when the concentration is (10^{-4}) M and (a_{RB}) is the area under the RhB fluorescence curve and its value is (117.6 cm1), either (a) represents the area under the curve required for the compound in this search.

The spectrum of the molecular fluorescence F(ύ) gives the relative fluorescence intensity at wave-number (ύ), this is related to the quantum efficiency by the following equation [65]:

$$q_{fm} = \frac{\tau_f}{\tau_{fm}} \int_0^{\infty} F(\acute{\upsilon})\, d\acute{\upsilon} \qquad (2\text{-}9)$$

It is also possible to use the fluorination quantum yield (Φ_F) to calculate the relationship between the space of the fluorescence spectrum and the space of the absorption spectrum [67]:

$$\Phi_F = \frac{\int F(\acute{\upsilon})d\acute{\upsilon}}{\int \varepsilon(\acute{\upsilon})d\acute{\upsilon}} \tag{2-10}$$

Where $\int F(\acute{\upsilon})d\acute{\upsilon}$ is the area under the curve fluorination and $\int \varepsilon(\acute{\upsilon})d\acute{\upsilon}$ is the area under the curve absorption.

2.5 Optical Properties

Optical property refers to a material’s response to exposure to electromagnetic radiation and, in particular, to visible light. Its divided into two types: Linear optical properties and nonlinear optical properties.

2.5.1 Linear optical properties

For information about the internal structure of matter and the nature of its ties must know transmittance and absorbance and the reflectivity of the electromagnetic beam incidence on the material, for example, power packs and quality of transitions within the material identified studying the ultraviolet spectrum, but to see the area of the operation involving the use of materials applications must study the visible spectrum [68].

2.5.1.1 Linear absorption coefficient

The decrease rate in radiation energy or by the intensity to the distance unit in the direction of the wave inside the medium is described as the following [69,70]:

$$\alpha_o = \frac{\ln(\frac{1}{T})}{t} \qquad (2\text{-}11)$$

Where (α_o) is the linear absorption coefficient and (t) is the thickness and its value is (1cm). Absorption coefficient (α_o) depends on incident photon energy (hυ).

2.5.1.2 Linear refractive index

Light that is transmitted into the interior of transparent materials experiences a decrease in velocity, and, as a result, is bent at the interface; this phenomenon is termed refraction. The index of refractive (n) of a material is defined as the ratio of the velocity in a vacuum (c) to the velocity in the medium (v), or:

$$n = \frac{c}{v} \qquad (2\text{-}12)$$

The magnitude of (n) will depend on the wavelength of the light. Not only does the refraction index affect the optical path of light, but also, it influences the fraction of incident light that is reflected at the surface. Because the retardation of electromagnetic radiation in a medium results from electronic polarization, the size of the constituent atoms or ions has a considerable influence on the magnitude of this effect generally, the larger an atom or ion, the greater the electronic polarization, the slower the velocity, and the greater the index of refraction. The linear refractive index obtained from equation. The linear refractive index (n_o) obtained from equation [51,69]:

$$n_o = \frac{1}{T} + [\left(\frac{1}{T^2} - 1\right)]^{1/2} \qquad (2\text{-}13)$$

2.5.1.3 Extinction coefficient

It is the quantity of energy that absorbed by the electronics valance band at the incident beam on the matter. The extinction coefficient (K) given by following equation [71,72]:

$$k = \frac{\alpha_o \lambda}{4\pi} \tag{2-14}$$

Where (λ) is the wave length of the incident beam. The extinction coefficient represents the amount of attenuation of an electromagnetic wave that is traveling in a material, where it values depend on the density of free electrons in the material and also on the structure nature [73].

2.5.1.4 Optical Energy gap

The energy gap of a material is the minimum energy needed to move an electron from its bound state within an atom to a free state, where the electron can be involved in conduction. The lower energy level of a material is called the valence band, and the higher energy level where an electron is free to ramble is called the conduction band. So the energy gap (often symbolized by E_{gap} or E_g) is defined as the energy difference between the conduction and valence bands [74].

If the photon energy (hν) is equal or more than energy gap (E_g) then, the photon can interact with a valence electron, elevates the electron into the conduction band and creates an electron–hole pair. The maximum wavelength (λ) of the incident photon which creates the electron–hole pair is defined as [75]:

$$\lambda = \frac{hc}{E_g} = \frac{1240}{E_g(eV)} \tag{2-15}$$

Electronic transition between the valence and conduction bands resulting from The absorption of radiation is divided into direct and indirect transition as shown in Figure (2.3) [76].

Direct transition happens when the bottom of conduction band is exactly over the top of valence band. This means that they have the same value of wave vector i.e. ($\Delta k=0$) in this state the absorption appears when ($h\upsilon = E_g$) . This transition type required to the laws of conservation in energy and momentum. These direct transitions have two types [77]:

a) Direct allowed transition

This transition happens from the top points in the valence band and the bottom point in the conduction band, as shown in Figure (2.5a).

b) Direct forbidden transitions:

This transition happens from near top points of valence band and near the bottom points of conduction band, as shown in Figure (2.5b).

The photon energy dependence of the absorption coefficient can be described by [77]:

$$\alpha h\upsilon = B(h\upsilon - E_g)^r \qquad (2\text{-}16)$$

Where (E_g) is the energy gap between direct transition, (B) is constant depended on type of material and (r) is exponential constant depended on type of transition (r =1/2 for the allowed direct transition, r =3/2 for the forbidden direct transition).

In indirect transitions type, the bottom of conduction band is not over the top of valence band, in curve (E-k). The electron transits from valence band to conduction band is not perpendicularly where the value of the wave vector of electron before and after transition is not equal ($\Delta k \neq 0$). This transition type happens with helpful of particle called "Phonon", for conservation of the energy and momentum law. There are two types of indirect transitions [78]:

a) Allowed indirect transitions

These transitions happen between the top of valence band and the bottom of conduction band which is found in the difference region of (k-space) as in Figure (2.5c).

b) Forbidden indirect transitions:

These transitions happen between near points in the top of valence band and near points in the bottom of conduction band, as shown in Figure (2.5d).

The photon energy dependence of the absorption coefficient can be described by [76]:

$$\alpha h\upsilon = B(h\upsilon - E_g + E_{ph})^r \qquad (2\text{-}17)$$

Where (E_{ph}) is the energy of phonon, is (+) when phonon absorption, and (-) when phonon emission. (r = 2 for the allowed indirect transition, r = 3 for the forbidden indirect transition).

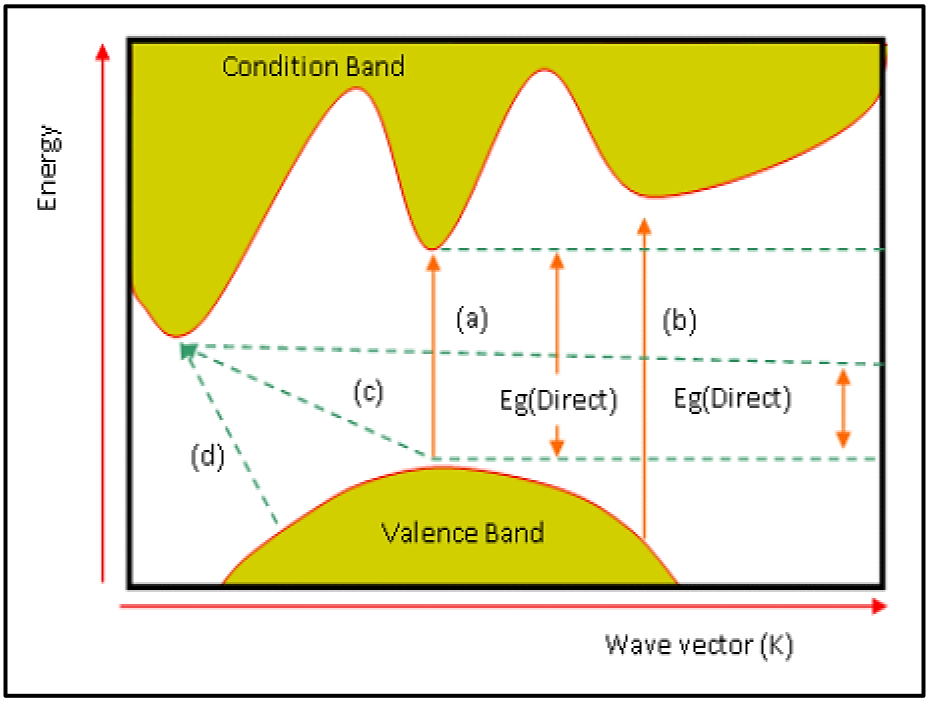


Figure (2.3) The electronic transition types [76]

(a) allowed direct transition. (b) forbidden direct transition.

(c) allowed indirect transition. (d) forbidden indirect transition.

2.5.1.5 Dielectric constant

Dielectric constant can be defined as the ratio of the absolute permittivity of a substance to the absolute permittivity of free space, the dielectric constant exhibits the liquid polarity [79]. A higher dielectric constant of the solvent correlates with a higher ability of the solvent to dissolve salts. The dielectric constant of the solvent also affects interactions in solution that involve ions and polar molecules, decreasing the intermolecular energy when the dielectric constant increases [80].

The real and imaginary parts follow the same pattern and the values of the real part are higher than the imaginary part [81].

$$\varepsilon = \varepsilon_{\mathrm{real}} - \mathrm{i}\varepsilon_{\mathrm{im}} \tag{2-18}$$

The real and imaginary parts of the complex dielectric constant are expressed as [81]:

$$\varepsilon_{\mathrm{real}} = \mathrm{n}^2 - \mathrm{K}^2 \tag{2-19}$$

$$\varepsilon_{\mathrm{im}} = 2\mathrm{nK} \tag{2-20}$$

Where (ε_{real}) and (ε_{im}) are the real and imaginary components of the complex dielectric constant, respectively.

2.5.2 NonLinear optical properties

The nonlinear properties of organic dye molecules are currently being explored with great interest, and it is important from the point of view of understanding their photophysics and for realizing the potential for using these molecules in applications like optical processing and optical limiting. The nonlinear refractive index is a very important parameter in designing optical devices [82].

Nonlinear Optics (NLO) is the study of all the phenomena that occur from the interaction of intense light with matter. The interaction with a nonlinear optical material causes a modification of the optical properties of the system. Typically only laser light is sufficiently intense to generate NLO phenomena. NLO interactions cause changing in frequency, phase, polarization or path of incident light, and are ‘nonlinear’ because the response of a system to the applied optical field depends in a nonlinear manner upon the strength of the optical field [83].

Typically, when light is absorbed by matter, the energy of a photon is resonant with an energy difference between an occupied electronic state and a higher electronic state. In photon absorption, the material responds linearly to the applied optical feld. i.e., when the applied electric field induces a nonlinear (non harmonic) displacement of charged particles (electrons) in a molecule. The displacement of the charges produces polarization (P) of a medium, which includes nonlinear, with respect to the electric field, terms. When light propagates through a medium, it induces displacement of the charge distribution (either bound electrons of the molecules or electron gas of metals) because of the electric component of the Lorentz force. The contribution from the weak magnetic component is neglected in the linear approximation. electric dipole moment, which oscillates with the frequency of the applied field in the linear approximation. The induced dipole moments add up to generate the polarization of the medium, in other words, the polarization (P) that is induced by the applied field can be written as follows [84]:

$$P = \varepsilon_o \chi E \qquad (2\text{-}21)$$

Where (E) is the magnitude applied electric field, (ε_o) is the permittivity of free space, and (χ) is the linear susceptibility of the medium.

The total light absorbed by a medium is proportional to product of the light intensity and the medium's absorption coefficient. The intensity is proportional to the magnitude squared of the electric field, so the response of the medium to an applied field need not be linear, in which case, we can write more generally that [85]:

$$P = \varepsilon_o(\chi^1 E + \chi^2 E.E + \chi^3 E.E.E + \cdots) \qquad (2\text{-}22)$$

Where $\chi^{(1)}$ is the first-order (linear) susceptibility tensor and $\chi^{(2)}$ is the second-order (nonlinear) susceptibility tensor, etc. It can be rewrite the polarization as follows:

$$P = P^1 + P^2 + P^3 + \cdots \qquad (2\text{-}23)$$

and so on. $P^{(1)}$ is known as the first-order polarization and $P^{(2)}$ is the second-order polarization, etc..

Organic dyes are the most attractive optical materials exhibiting large third-order nonlinear optical properties. NLO properties of organic dye molecules have been the subject of numerous investigations. Several experimental techniques currently available to measure the third-order NLO parameters ; One of the most important techniques is Z-Scan technique [86].

The main idea of the Z-Scan technique is to measure the intensity change in incident Gaussian laser beam transmission intensity through the sample as a function of its position (Z-position) from the focus of the beam. The Z-Scan technique is based on the transformation of phase distortion to amplitude distortion during beam propagation. The working principle of Z-Scan technique is based on the motion of the sample along the so-called Z-axis from (–Z) to (+Z) through the focus of Gaussian laser beam. The motion of the sample across the focused beam exposes it to a varying irradiance (intensity) level reaching its maximum value at the focus point. Transmitted beam is collected by means of two detector arrangements: closed aperture (CA) in order to recognize the sign and measure nonlinear refractive index and open aperture (OA) in order to measure nonlinear absorption coefficient as illustrated in figure (2.4) [87,88].

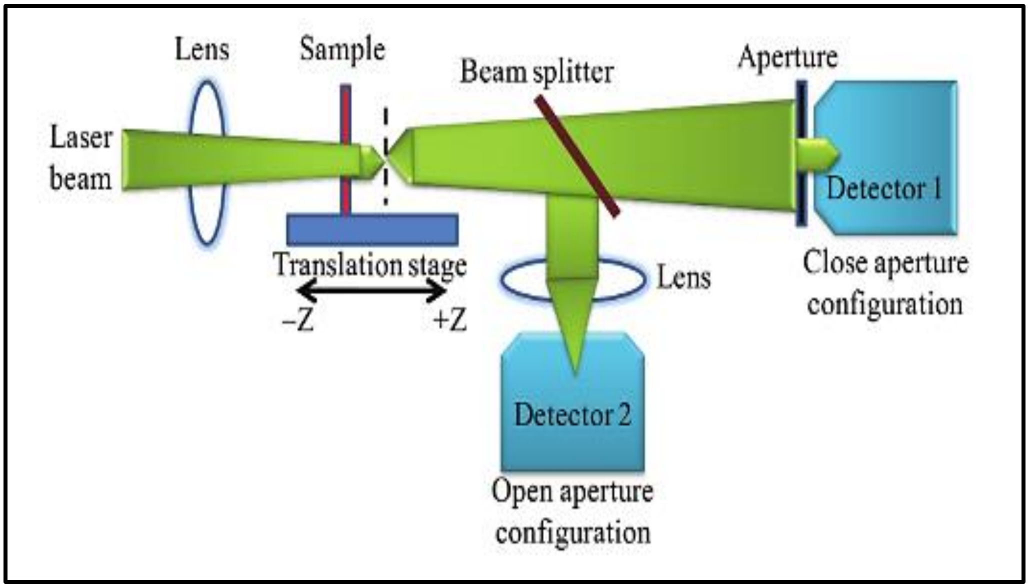


Figure (2.4): Schematics of experimental setup used for the closed-and open-aperture Z-Scan [87].

2.5.2.1 Nonlinear absorption coefficient

In the OA Z-Scan performed to measures nonlinear absorption coefficient, where measures the change in intensity of a beam, the aperture removed from the experimental setup (or fully open-aperture) that is, aperture (S=1) is insensitive to nonlinear refraction and the entire laser beam transmitted through the sample is collected by a photo-detector, so the measurements are sensitive only to nonlinear absorption. The laser beam transmission is measured as a function of the sample position (Z) with respect to the focal plane. The change in intensity is caused by multi-photon absorption in the sample as it travels through the beam waist [89].

Sample transmittance decreases (increases) as sample position (Z) gets closer to the focus point of the lens with minimum (maximum) value of the transmittance at the focal point (Z=0) , then it increases (decreases) as the sample moves away from the focus and reaches its linear behavior at far (+Z) position . If the transmittance is minimum at the focus (valley) this indicates the existence of two-photon absorption (TAP) or (RSA) with a positive type of nonlinear absorption. However, when the transmittance is maximum at the focus (peak), this indicates the presence of saturable absorption (SA) with negative type of nonlinear absorption. [90].

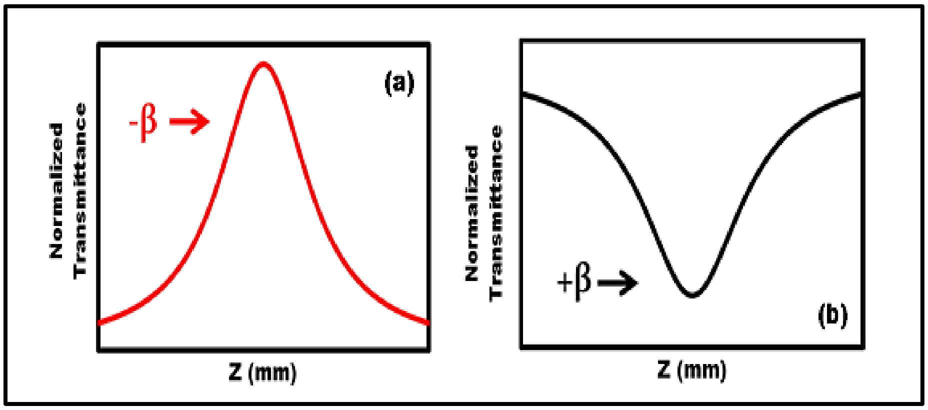


Figure (2.5): Open aperture Z-Scan traces (a) saturable absorption and (b) reverse saturable absorption curves.

Nonlinear light absorption is a basic phenomenon of the interaction between the light and the matter. The nonlinear absorption can be described as the absorption coefficient of the medium being a function of the light intensity. When a laser beam propagates in a medium, if the interaction between light and matter is far away from the resonance, it may exists two kinds of absorptions in the medium at the same time: the single-photon absorption (α_o) and the two-photon absorption (β). We denote the total absorption coefficient of medium as (α) [91]:

$$\alpha = \alpha_o + \beta I \qquad (2\text{-}24)$$

The two-photon absorption coefficient, can be calculated by using the following relation [92]:

$$\beta = \frac{2\sqrt{2}}{I_o L_{eff}} \Delta T \tag{2-25}$$

Where (ΔT) is the normalized transmittance difference between peak at the focal point (Z=0) in the open-aperture Z–Scan normalized transmittance curve and the baseline, I_o is the intensity of the laser beam at focus (Z=0), and given by [93]:

$$I_o = \frac{2P_o}{\pi \omega_o^2} \tag{2-26}$$

Where (P_o) is the laser input power, (ω_o) is the beam radius at the focal point, (L_{eff}) is the effective length of the sample and given by [94]:

$$L_{eff} = 1 - \frac{\exp(-\alpha_o L)}{\alpha_o} \tag{2-27}$$

Where (L) is the true sample length.

At low light levels, the absorption coefficient of a medium does not depend on of the input light intensity. At high intensities, however, several phenomena can take place that can modify this behavior. For instance, absorption can become saturated as the excited state population increases. Alternatively, the excited states can absorb photons, sometimes even stronger than the ground state. Another possibility is that of two or more photons getting absorbed in a single event. All these phenomena will change the transmittance of the medium at high intensities, causing a deviation from the Beer-Lambert law. This change in transmittance of a material with input light intensity or flounce is generally known as nonlinear absorption [95].

2.5.2.2 Nonlinear refractive index

The standard "closed aperture" Z-Scan (i.e. aperture is placed in the far field) for determining nonlinear refraction as shown in figure (2.6), where the sample is moved along the propagation direction (Z) while keeping the input pulse energy fixed. The normalized transmittance of the sample through the aperture is monitored in the far field as a function of the position (Z) [96].

The size of the aperture is signified by its transmittance (S). A qualitative physical argument that explains the transmittance variations in the Z-Scan experiment can be given as follows: Starting the scan from a distance far away from the focus (negative Z), the beam irradiance is low and negligible nonlinear refraction occurs leading to linear transmittance. As the sample is brought closer to the focus, the beam irradiance increases leading to self-lensing in the sample. A negative self-lensing (self-defocusing) prior to focus tends to collimate the beam and reduce the diffraction leading to a smaller beam at the aperture and an increased transmittance. As the scan continues and the sample crosses the focal plane to the right (positive Z) this means that a greater index, and hence the larger phase retardation, is induced in the on-axis center than in the wings of the beam, the same self-defocusing effect will tend to augment diffraction and reduce the aperture transmittance. A prefocal transmittance maximum (peak) and a post focal transmittance minimum (valley) will be, the Z-Scan signature of a negative nonlinearity , it have an inverse situation, while a positive one, following the same analogy, will give rise to an opposite valley-peak configuration, as shwon by the figure (2.6). The nonlinear focusing has the effect of creating a positive ($n_2>0$) or negative ($n_2<0$) lens in the medium that tends to focus or defocus slightly the beam [97, 98].

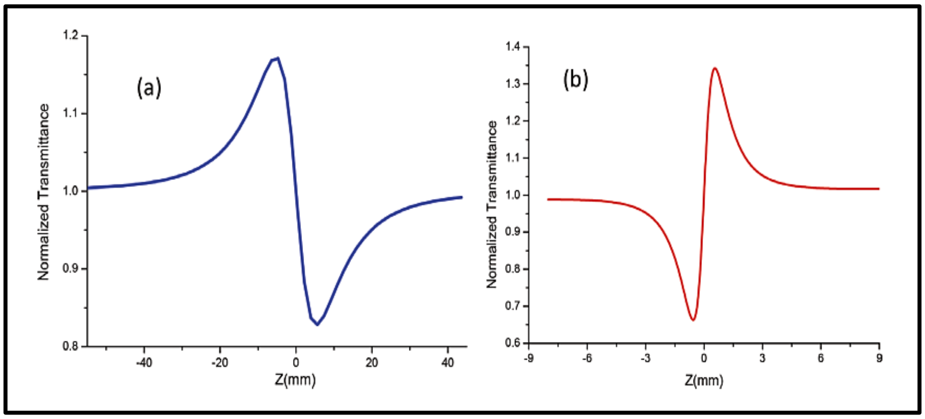


Figure (2.6): Closed-aperture Z-Scan normalized transmittance curve (a) negative n_2 and (b) positive n_2 [87].

The refractive index is one of the fundamental properties of a material. It is closely related to the electronic polarizability of ions and the local field inside the material. The evaluation of the refractive indices of optical materials is important for applications in integrated optics devices such as switches, filters and modulators, etc. Thus, the refractive index of a material is the key parameter for device design [99].

Dependent nonlinear refractive index on intensity can be determined as follows [100]:

$$n = n_o + n_2 I \qquad (2\text{-}28)$$

Where (n) the total refractive index and (n_2) is the nonlinear refractive index.

The nonlinear refractive index is calculated from the peak to valley difference of the normalized transmittance by the following formula [101]:

$$n_2 = \frac{\Delta\Phi_O}{I_o L_{eff} K} \qquad (2\text{-}29)$$

Where (K) is the wave number ($K=2\pi/\lambda$) and (λ) is the laser wavelength. ($\Delta\Phi_o$) is the on-axis phase shift of the laser beam traversing the medium. This phase shift is related to the difference between the peak and valley transmittances (T_p and T_v) for the closed-aperture Z–Scan ($\Delta T_{P\text{-}v}=T_p-T_v$) according to the following relation [102]:

$$\Delta T_{P-V} = 0.406(1-s)^{0.25}|\Delta\Phi_o| \tag{2-30}$$

Where (S) denotes aperture linear transmittance, and given by [102]:

$$s = 1-\exp(\frac{-2r_o^2}{\omega_o^2}) \tag{2-31}$$

In the linear region, (r_o) is the diameter of the slit.

2.5.2.3 Saturable Light Absorption

Saturable absorption (α) is a nonparametric nonlinear optical process in which the absorption of an optical medium decreases with increasing the pump fluence beyond a threshold value, in which the total intensity-dependent absorption coefficient:

$$\alpha(I) = \alpha_o \frac{1}{1+{}^{I}/_{I_s}} + \beta I \tag{2-32}$$

Where the first term describes negative nonlinear absorption such as saturable absorption, the second term describes positive nonlinear absorption such as reverse saturable absorption or two-photon absorption and (I_s) are laser saturation intensity [103,104].

2.5.2.4 Two Photon Absorption

Two–photon absorption (TPA) is one of the most basic radiation–matter interaction mechanisms. Two–photon absorption is a nonlinear process that involves an optical excitation in a material system from the ground to an excited state by the simultaneous absorption of two incident photons. Unlike the linear absorption case, the TPA cross section (σ) is linearly proportional to the incident source intensity

$$\sigma = \beta I \tag{2-33}$$

Because the transition rate (R) from the ground state to the excited state is proportional to the product of the absorption cross section and incident intensity, the TPA rate is:

$$R = \frac{\beta I^2}{\hbar\omega} \tag{2-34}$$

In most materials, attenuation of the incident beam by the (β) term is negligible until very high intensities are achieved in the illuminated materials [105,106]. Two-photon absorption processes are based on the simultaneous absorption of two photons at a wavelength that is two times longer than that corresponding to single-photon excitation [107].

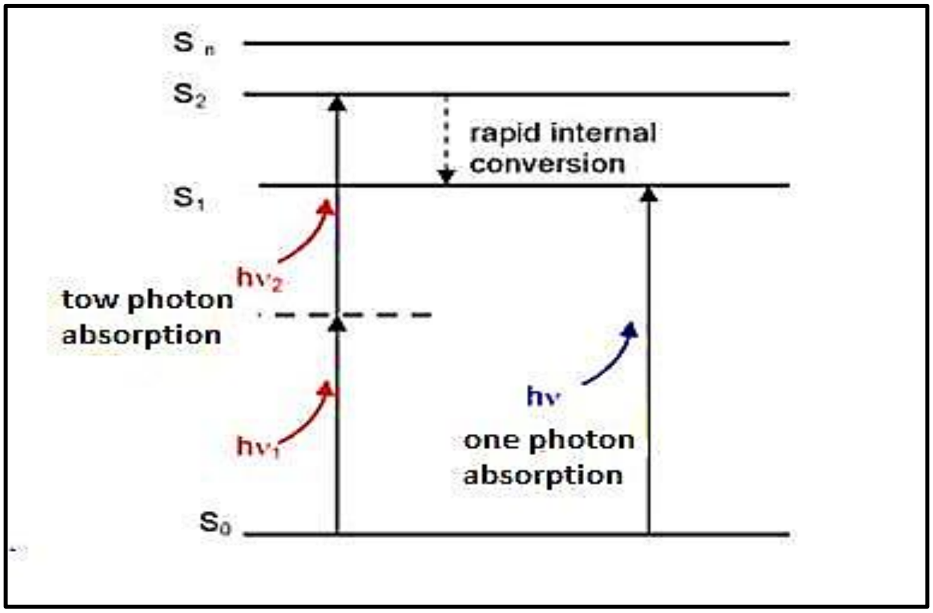


Figure (2.7): Jablonski for two photon and one photon absorption [108].

2.5.2.5 Kerr Effect

Kerr effect is a third-order non-linear process. It is change refractive index in a medium by an applied electric field. In Kerr effect, the intensity of light dependence on the refractive index which leads to a much of an interesting nonlinear effect, and the refractive index of the medium varies linearly with the square of the electric field. Kerr effect give rise to an increase of the refractive index with intensity and a resulting focusing nonlinear lens [109,110]. Where (n_2) in the equation (2-28) often referred to as the Kerr coefficient [111].

2.5.2.6 Self-Focusing

Self-focusing of light is the process in which an intense beam of light modifies the optical properties of a material medium in such a manner that the beam is caused to come to a focus within the material . Here, it have assumed that (n_2) is positive. As a result, the laser beam induces a refractive index variation within the material with a larger refractive index at the center of the beam than at its periphery. Thus the material acts as if it were a positive lens, causing the beam to come to a focus within the material. More generally, one refers to self-action effects as effects in which a beam of light modifies its own propagation by means of the nonlinear response of a material medium [112,113].

Chapter Three

Experimental Part

3.1 Introduction

This chapter describes the preparation method of RhB dye solution before and after addition, and the instruments used for characterization of the material.

3.2 Chemical Materials

The materials that were used for preparation of the samples, include: organic laser dyes and suitable solvents are described below.

3.2.1 Rhodamine B dye

RhB[9-(2-carboxyphenyl)-6-diethylamino-3xanthenylidene]diethyl ammonium chloride is a cationic xanthene dye. Molecular structure of this dye shown in the figure (3.1) [114,115].

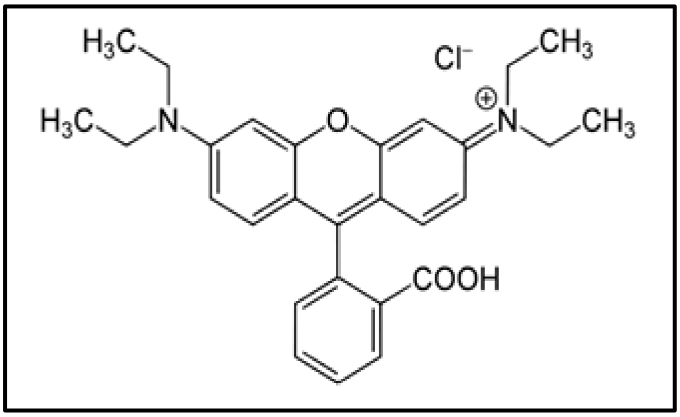


Figure (3.1): Molecular structure of rhodamine B dye [114].

RhB dye is one of the most commonly used in various spectroscopic Studies. According to their spectral properties, it is broadly used in technology and science for lasing, specialy in dye lasers **[5].** The Physicochemical properties of this dye is presented in table (3.1).

Table (3.1): Physicochemical properties of RhB Dye.

Rhodamine B Dye	Description
Productive company	Sigma–Aldrich
Scientific name	Tetraethylrhodamine, Brilliant pink, Basic violet
Chemical formula	$C_{28}H_{31}N_2O_3Cl$
Molecular weight	479.01 g/mol
pH	3- 4 (10 g/L in H_2O, 20 °C)
Appearance	Powder or crystal
Colour	Bright-red to violet

3.2.2 Methanol solvent

Methanol is the simplest aliphatic alcohol. As a typical representative of this class of substances, its reactivity is determined by the functional hydroxyl group. Methanol is a colorless, neutral, polar liquid that is miscible with water, alcohols, esters, and most other organic solvents; it is only slightly soluble in fat and oil. Because of its polarity methanol dissolves many inorganic substances, particularly salts, the following table show Physicochemical properties of this solvent [116].

Table (3.2): Physicochemical properties of Methanol solvent.

The solvent	Description
Productive company	Analar company (England)
Scientific name	Methanol, Methyl alcohol, Carbinol, Sodium Methoxide
Chemical formula	CH_3OH
Molecular weight	32.04 g/mol
Boiling point	64.7 °C
pH	11 (20 g/L in H_2O, 20 °C)

3.2.3 Hydrochloric acid

Hydrochloric acid (HCl), also known as muriatic acid, is a solution of hydrogen chloride in water. hydrogen chloride under standard conditions is a colorless gas with a pungent odor and an extremely mordant effect on the mucous membranes of the respiratory system. a solution of hydrogen chloride in a polar solvent is a strong acid and, therefore, an aggressive reagent, Some Physicochemical properties of hydrogen chloride are given in below table [117].

Table (3.3): Physicochemical properties of hydrochloric acid.

The solvent	**Description**
Productive company	Sdfcl
Scientific name	Hydrogen chloride solution
Chemical formula	HCl
Molecular weight	36.46 g/mol
Boiling point	61 °C
pH	<1 (H_2O, 20 °C)

3.2.4 Acetic acid

Acetic acid (CH_3COOH) or also known as ethanolic acid is the simplest carboxylic acid that is responsible for the vinegar sour taste and its pungent smell. Pure acetic acid is colorless and a corrosive liquid with an irritating odor of vinegar. Acetic acid is classified as a weak acid that partially dissociate into component ions in aqueous solution. Acetic acid is a hydrophilic (polar) protic solvent which makes it miscible in all proportions with all polar and nonpolar compounds. The physical and chemical properties of acetic acid are shown in table (3.4) [118].

Table (3.4): Physicochemical properties of acetic acid.

The solvent	**Description**
Productive company	Macron
Scientific name	Ethanoic acid
Chemical formula	CH_3COOH
Molecular weight	60.05 g/mol
Boiling point	119 °C
pH	2.5 (50 g/L in H_2O, 20 °C)

3.2.5 Ammonia base

Ammonia (NH_3) is a colorless gas with a very sharp odor. Ammonia in this form is also known as ammonia gas or anhydrous (without water) ammonia. Ammonia gas can also be compressed and becomes a liquid under pressure. Ammonia is a chemical, It is made up of one part nitrogen (N) and three parts hydrogen (H_3) [119].

Table (3.5): Physicochemical properties of ammonia base.

The solvent	**Description**
Productive company	Scharlau
Scientific name	Ammonia aqueous, Ammonium hydroxide solution
Chemical formula	NH_3
Molecular weight	26 g/mol
Boiling point	-33.34 °C
pH	>12 (50 g/L in H_2O, 20 °C)

3.2.6 Sodium hydroxide base

Sodium hydroxide (NaOH) is a white and deliquescent solid. Impurities are sodium chloride (≤ 2%), sodium carbonate (≤ 1.0%) and sulfate (≤ 0.2%). The concentration of other impurities is less than (0.1%). NaOH is a strong alkaline substance that dissociates completely in water into the sodium ion (Na^+) and hydroxyl ion (OH^-) [120].

Table (3.6): Physicochemical properties of Sodium hydroxide base.

The solvent	**Description**
Productive company	Sigma
Scientific name	Caustic soda
Chemical formula	NaOH
Molecular weight (Mw)	40 g/mol
Boiling point	1,388 °C
pH	13.7 (H_2O, 20 °C)

3.3 Work Scheme

The experimental procedure has been shown in figure (3.2) as a block diagram of the main steps that are followed in this work. It includes the steps of preparation and measurements for used chemical materials whose characteristics are summarized in this chapter:

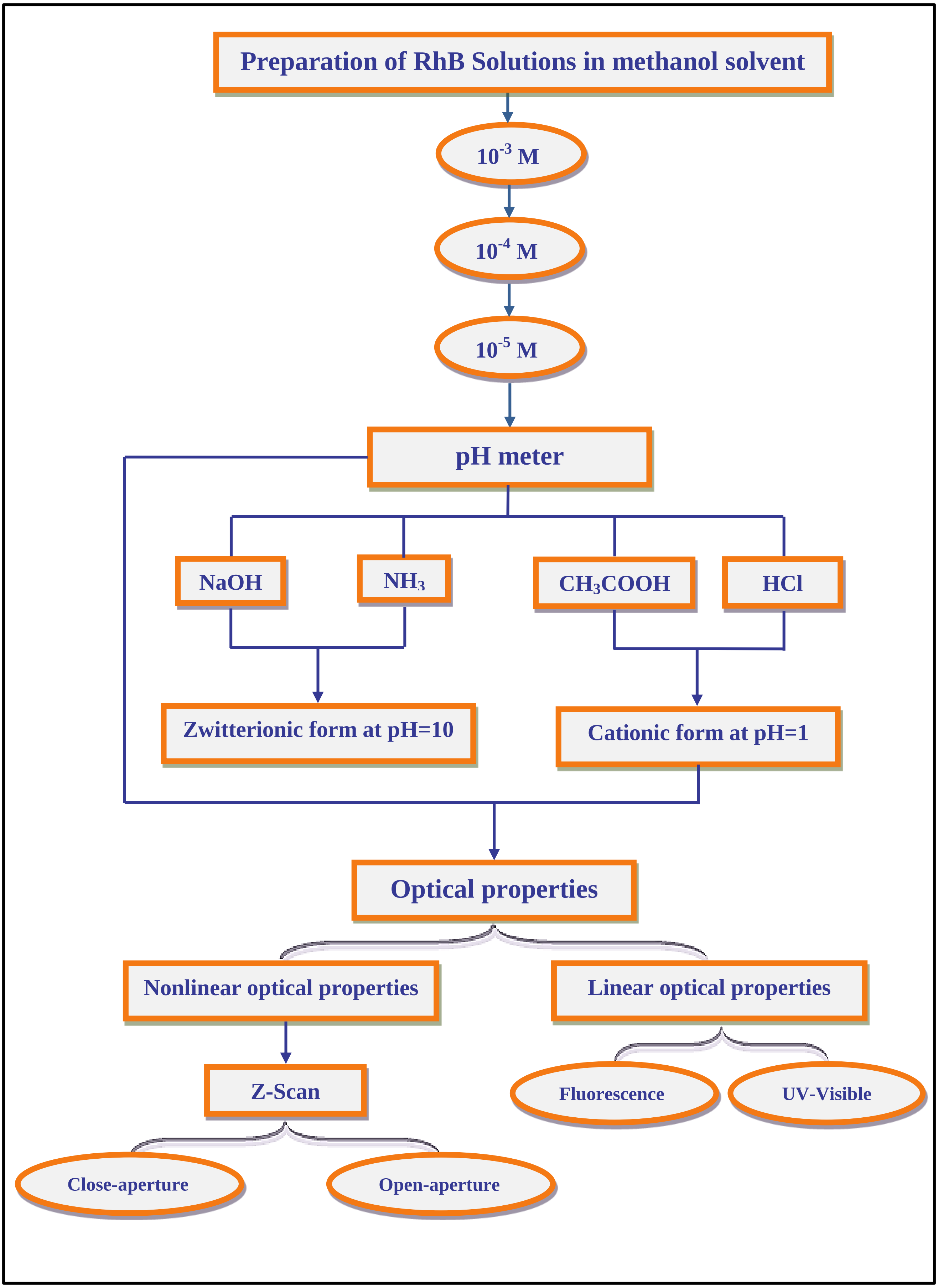


Figure (3.2): Schematic diagram of the experimental work.

3.4 Solutions Preparation

A mass of 0.0479 gm of RhB dye was added to a number of 250 ml glass bottles containing 100 ml. The mixing was stirred by using magnetic stirrer at room temperature to get a homogeneous solution.

Solutions of concentrations of 10^{-3},10^{-4} and10^{-5} M for organic dyes in Methanol solvent were prepared. The powder was weighted by using an electronic balance type (BL 210 S), Germany, having a sensitivity of four digits. Different concentrations were prepared according to the following equation [121]:

$$c = \frac{W\ X\ 1000}{M_W\ X\ V} \qquad (3\text{-}1)$$

Where, W: Weight of the dye dissolved in methanol solvent (g), Mw: Molecular weight of the dye (g/mol),V: Volume of the methanol solvent (mL) and C: The concentration of the dye (M). The prepared solutions were diluted according to the following equation[122].

$$C_1V_1 = C_2V_2 \qquad (3\text{-}2)$$

Where: C_1: Primary concentration, C_2: New concentration. V_1: The volume before dilution and V_2:The volume after dilution.

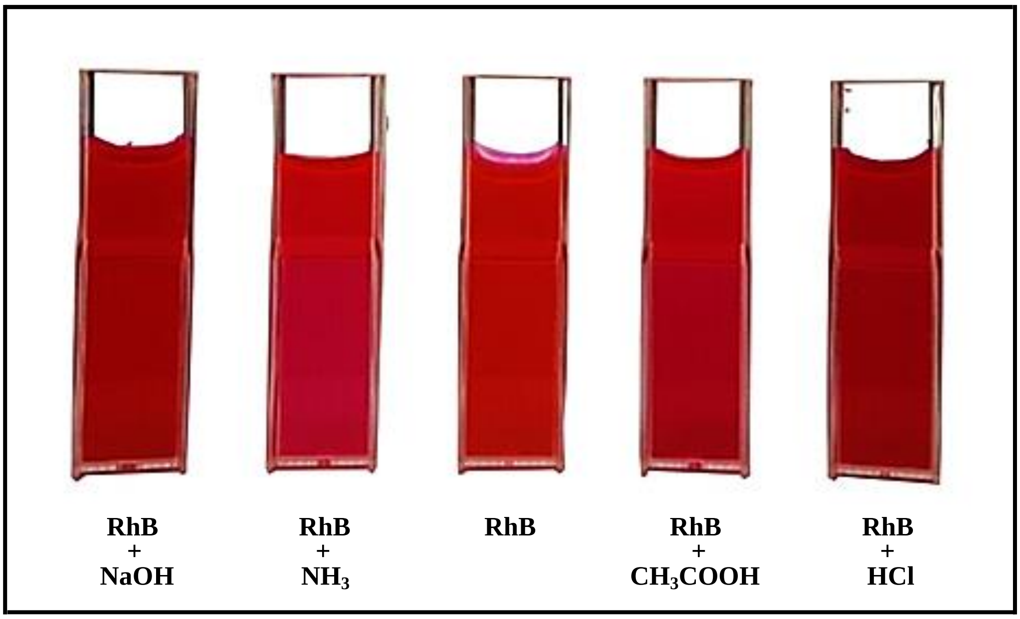


Figure (3.3): Liquid samples of RhB dye solution before and after addition at concentration (10^{-3} M).

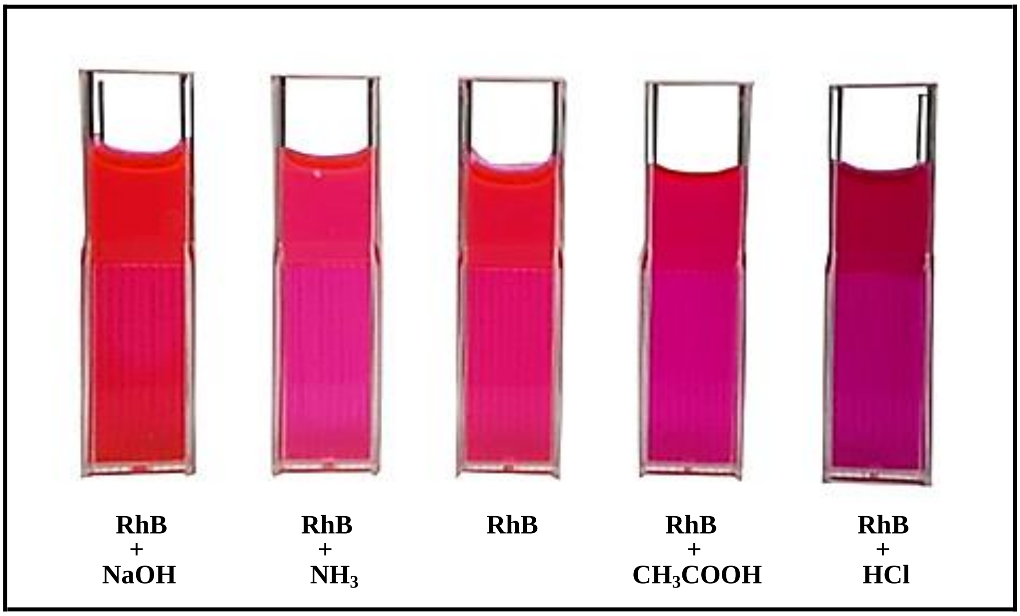


Figure (3.4): Liquid samples of RhB dye solution before and after addition at concentration (10^{-4} M).

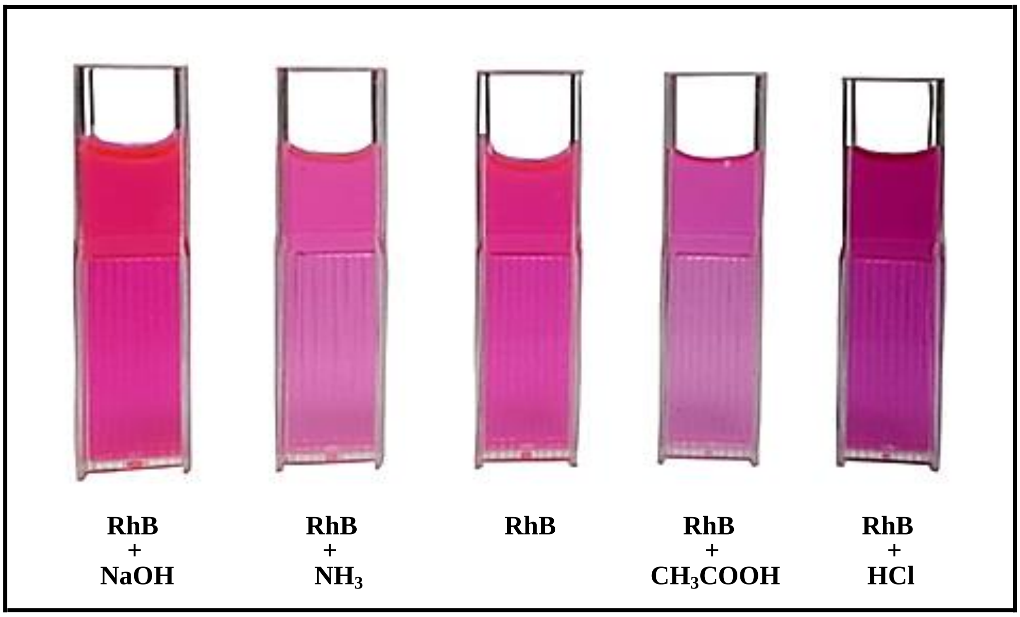


Figure (3.5): Liquid samples of RhB dye solution before and after addition at concentration (10^{-5} M).

3.5 The Effect of Solution pH and Ionic Strength on Dye

Since the quantity of additive affects critically the laser output power and efficiency, the number of drops was not adequate for use as a measure. Therefore, pH value was selected as a parameter because of its simplicity of adjustment and high reproducibility. [123]

The cationic form of RhB dye solutions was prepared by adjusted over the range (PH=1) once by adding trace of strong acid HCl, another one by adding (18 drops) of weak acid (CH_3COOH) to (18 ml) of dye solution . A trace of strong base NaOH (10 gm in 10 ml), one more time (15 drops) of weak base NH_3 were added to (18 ml) of dye solution for adjustment over the range (PH=10) to generate the zwitterionic form. The mixing was stirred by using magnetic stirrer at room temperature to get a homogeneous solution at room temperature.

3.6. Optical Properties Measurements

Experimental procedures and measurement techniques of optical characterization is described in the following paragraphs:

3.6.1 Linear optical properties

Linear optical properties included the absorption, transmission, linear absorption coefficient and refractive index measurements of RhB dye solution (before and after) addition.

3.6.1.1 UV-Visible absorption spectrophotometer

Linear optical properties were studied in the wavelength range of 200-800 nm by using UV-Visible shimadzu 1800 spectrophotometer which is present in the laboratory of Polymer at Physics Department, College of Science, University of Babylon. This spectrometer contains two light sources deuterium and tungsten lamp within the wavelengths range

(190–390) nm and (390–1100) nm of the spectrum respectively. The output data of wavelength, transmittance and absorbance are used in a computer program to deduce the optical energy band gap and fundamental optical edge and all optical constants, as shown in figure (3.6).

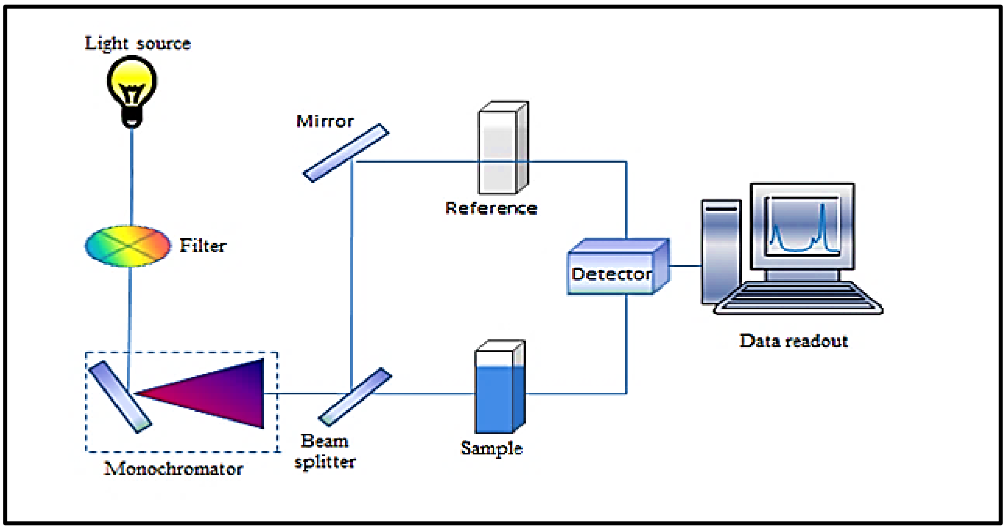


Figure (3.6): Schematic diagram of UV-Visible absorption spectrophotometer.

3.6.1.2 Fluorescence spectrophotometer

Fluorescence spectra was recorded by single beam spectrometer of Rhodamine B (pure and two forms) solution. Fluorescence emission was measured from the samples prepared at the section using spectro fluorophotometer type of (RF-5301pc Shimadzu) in the laboratory of thin films at Physics Department, College Education for Pure Science , University of Babylon. the sample were mounted cubic cell of quartz dimensions (1 x 1 x 5) cm at angle (90^o) with incident beam. This optical geometry was chosen to eliminate the effect of scattered incident radiation. The instrument computerized and operates in the wavelength range (220-900) nm. The fluorimeter has dedicated computer which control instrumental operating (excitation and emission wavelength, scan, monochromator slit width, detector parameter) and the acquisition of spectral data, as shown in Figure (3.7).

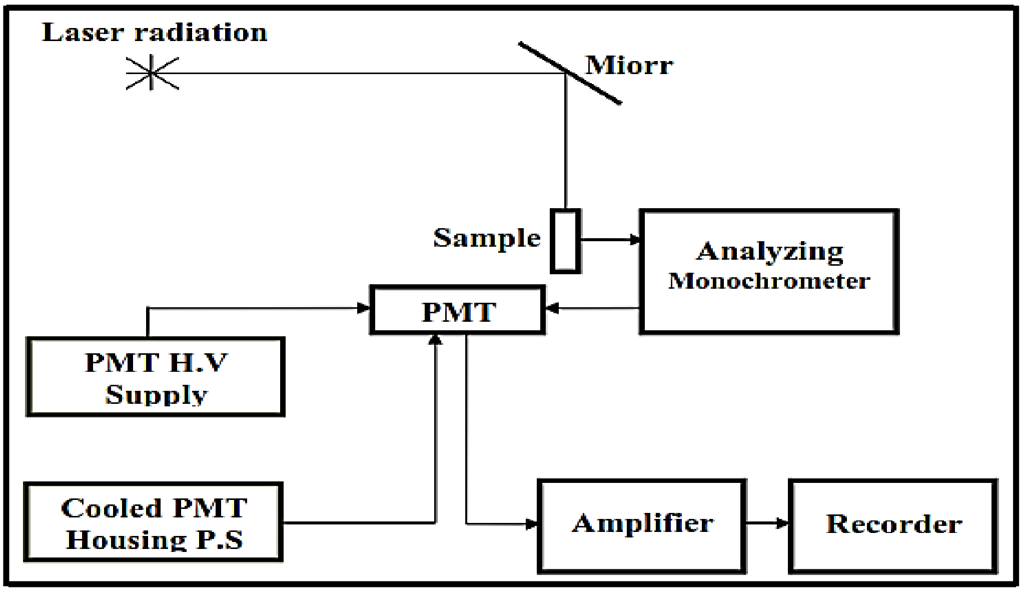


Figure (3.7): Schematic diagram of the fluorescence spectrophotometer.

3.6.2 Nonlinear optical properties

Nonlinear optical properties of Rhodamine B (pure and two forms) included nonlinear absorption coefficient and refractive index measurements by using Z-Scan Technique.

Z-Scan measurements were performed in two parts, closed and open aperture. Each part was employed using continuous wave (CW) diode pump solid state blue laser at wavelength (457 nm) and (112 mW) power, which its characteristics showed in the following table.

Table (3.7): Characterization of 457 nm DPSS laser.

Properties	**Model**
Wavelength (nm)	457 nm
Output power (mW)	142.5 mW
Transverse mode	TEM00
Operating mode	CW
Power stability (rms, over 4 hours)	5.71 %
Beam divergence, full angle (mrad)	1.8
Beam diameter at 1/e2 (mm)	X: 1.883 nm Y: 1.285 nm
Power Supply	(100-240) volt

The closed-aperture Z-Scan was used to measure the nonlinear refractive index, while the open-aperture was used to measure the nonlinear absorption coefficient. The beam was focused by using a convex lens (f =15 cm), and the beam waist have been measured at the focus equal to (0.025) cm. The laser intensity at the focal point is (20.408×103) mW/cm^2, the sample was moved along the Z-axis.

The transmittance through the sample is recorded as a function of sample position. Figure (3.8) shows the open-aperture and closed-aperture Z-Scan setup.

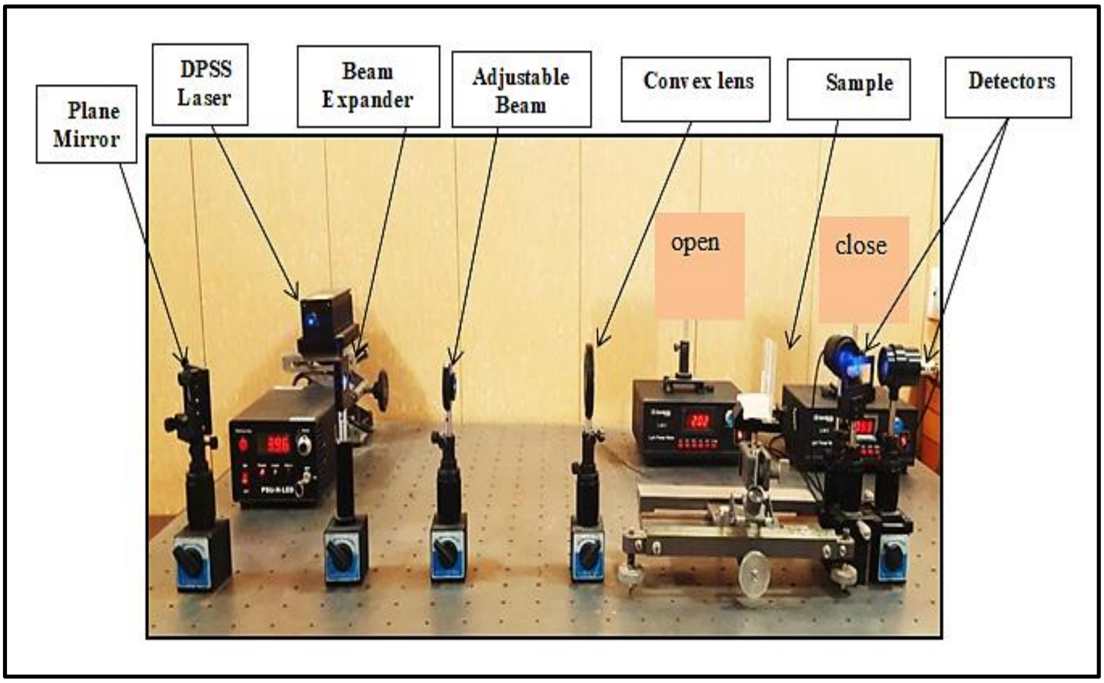


Figure (3.8) : Z-Scan set-up.

3.7 pH Meter

A pH meter is a scientific instrument that measures the hydrogen-ion activity in solutions, indicating its acidity or alkalinity expressed as pH.

pH were measured by using pH Meter, pw 9421, philips, England, as shown in figure (3.9),This device is present in the laboratory of Advanced Analytical Laboratory at chemistry Department, College of Science, University of Babylon. The most important component of a typical pH meter is its special measuring probe (a glass electrode), which is connected to an electronic meter that measures and displays the pH reading. The electrode, or probe, are inserted into the solution to be tested. All pH meters are calibrated against buffer solutions of known hydrogen ion activity. Very precise measurements necessitate that the pH meter is calibrated before each measurement. More typically calibration is performed once per day of operation. Calibration is needed because the glass electrode does not give reproducible electrostatic potentials over longer periods of time.

Chapter Four

Results and Discussion

4.1 Introduction

This chapter includes results and the analysis of spectral, linear and nonlinear optical properties of prepared RhB dye solution before and after addition with different concentrations at room temperature.

4.2 Linear Optical Properties

The linear optical properties were investigated of RhB dye solution before and after addition at different concentrations (10^{-3},10^{-4} and 10^{-5}) M in methanol solvent by using UV-Visible spectrophotometer which recorded the absorption spectra, and by the fluorescence spectrophotometer which recorded the fluorescence spectra. Also some optical constants have been determined for the same concentrations.

4.2.1 pH effect

Rhodamine B is a xanthene dye whose optical properties depend on several factors, among which is the pH value [124]. pH have been measured of RhB dye solution before and after addition at room temperature with different concentrations as tabulated in table (4.1).

Table (4.1): pH value of pure RhB dye solution at different concentrations.

Concentration	**pH**
10^{-3}	2.7
10^{-4}	5
10^{-5}	6.3

It show from the range of pH in this table that RhB dye is acidity dye (cationic dyes) which is largely applied in industry as a dye for paper, silk, wool, jute, leather, and cotton [125]. These values show the correlation of the pH of the solute as a function of concentration. When pH of the RhB dye solution decreases, an increase in the concentration and the acidity is observed [126].

4.2.2 Absorbance spectra

The absorbance spectra for RhB dye solution before and after addition at different concentrations (10^{-3}, 10^{-4} and 10^{-5}) M in methanol solvent at room temperature was recorded and shown in Figure (4.1).

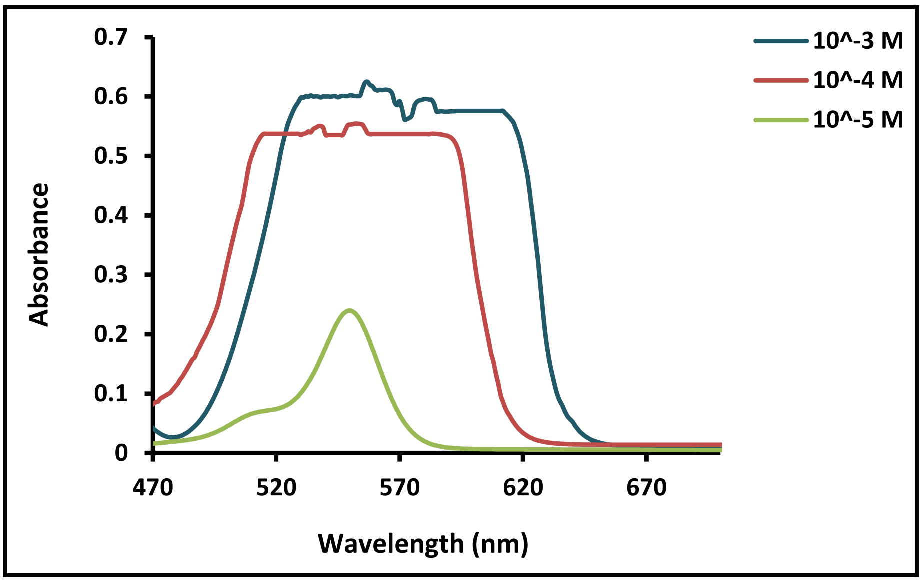


Figure (4.1): Absorbance spectra as a function of wavelength of pure RhB dye solution at different concentrations.

It could be seen that there is an absorption band in the visible light region called Q-band, which originates from the (π– π *) transitions from HOMO to the LUMO along the longest dimension of the conjugated system [127,128].

It has be shown that maximum absorption appears at higher concentration as well as the red shift, this is due to the fact that an increase in concentration produce an increase in number of molecules in volumetric unit which effect the energy state. This increase in concentration produce an increase in perturbation field of the molecules and while at the concentration decreases the relative intensity decrease which is in agreement with Beer–Lambrat law [129]. On the other hand, they are attributed to the change of RhB from its neutral form to the cationic one , this theory is based on the decreasing of pH produced when dye concentration increases, these finding has also reported in the literature [33].

The charge of RhB can change from a zwitterion to cationic in response to pH [130]. When the pH is decreased (pH=1), a progressive shift of the absorbance spectra to lower energies (red shift) due to (π-π*) transitions, and an increase of the absorptivity (Hyperchromic shift) [21,131], as shown in the figures (4.2-4.4).

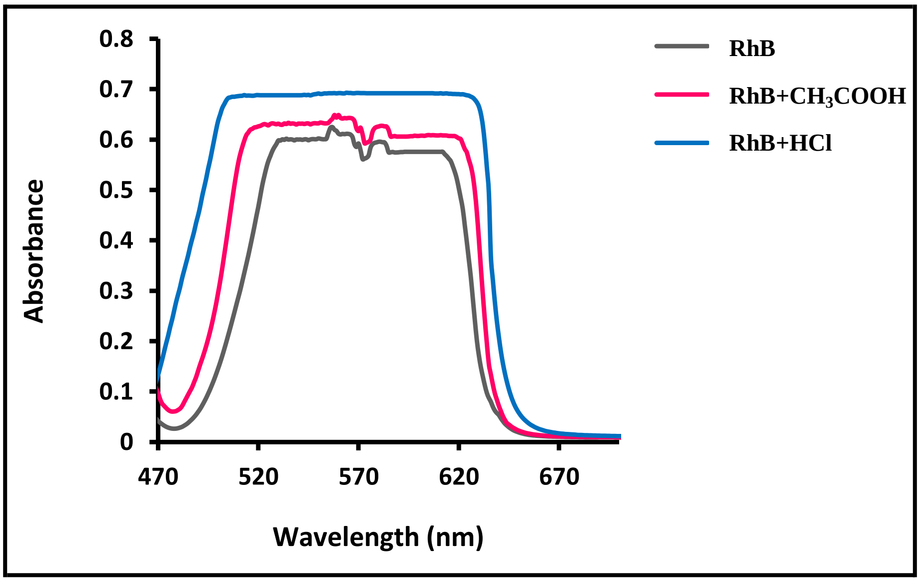


Figure (4.2): Absorbance spectra as a function of wavelength of cationic form for RhB dye solution at concentration (10^{-3}) M.

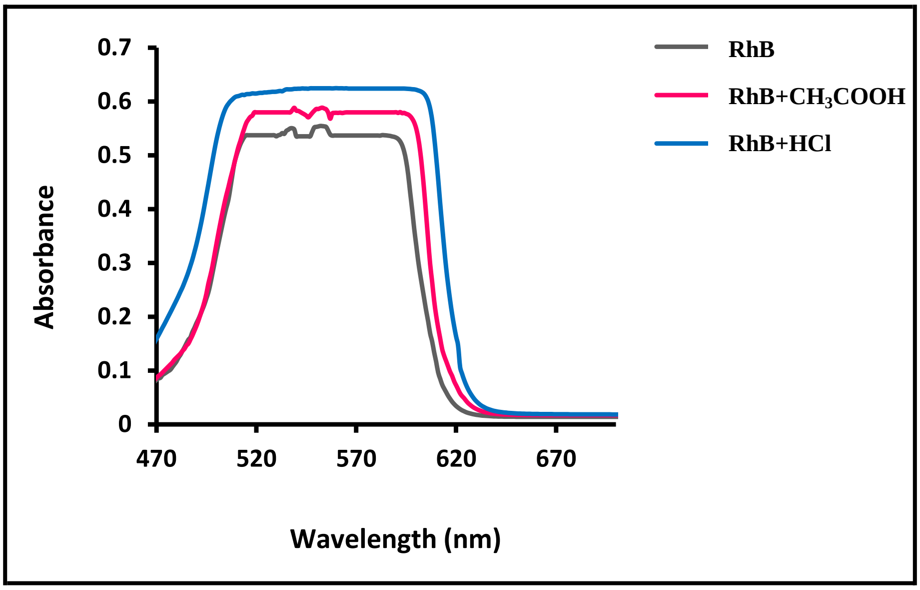


Figure (4.3): Absorbance spectra as a function of wavelength of cationic form for RhB dye solution at concentration (10^{-4}) M.

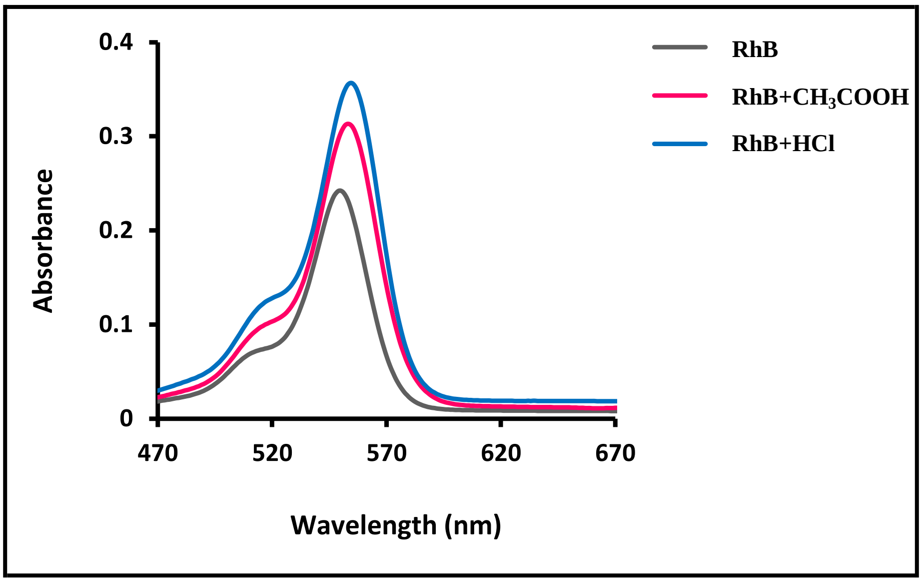


Figure (4.4): Absorbance spectra as a function of wavelength of cationic form for RhB dye solution at concentration (10^{-5}) M.

The red shift (bathochromic shift) in the absorbance spectra of cation relative to zwitterion has been ascribed to two molecular structural factors. One factor is the inductive effect of carboxyphenyl group through the ninth carbon atom of xanthene ring, where the inductive effect is strong of PhCOOH . Second factor is the weak electrostatic repulsion between carboxyphenyl group and xanthene conjugation system, where the electrostatic repulsion in zwitterion is stronger than in cation [128]. As well as the quaternary ammonium group of the protonated form of rhodamine B associates a chloride anion resulting in a red shift of the absorption band [132].

When pH increases (pH=10), observes a progressive shift of the absorbance spectra to higher energies (blue shift) and decrease of the absorptivity (hypochromic shift) [133], as shown in the figures (4.5-4.7).

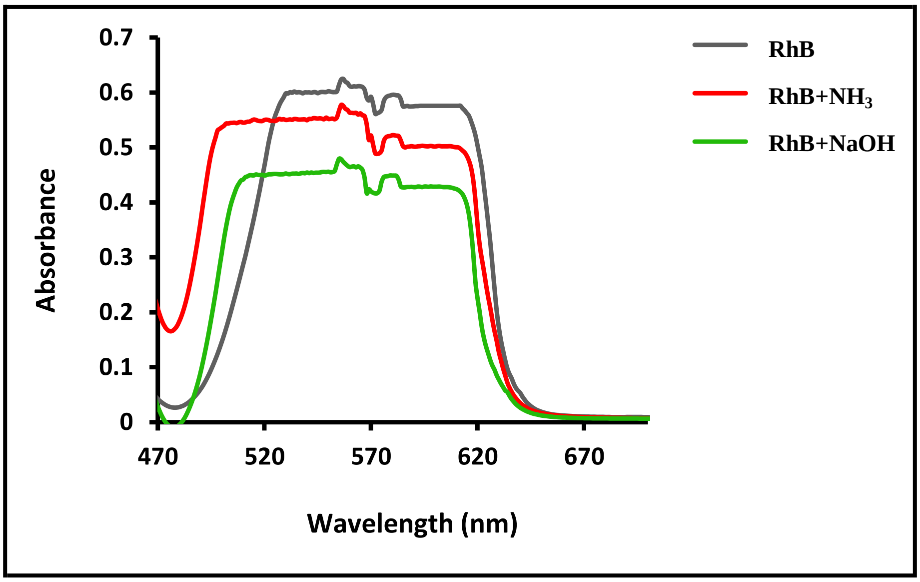


Figure (4.5): Absorbance spectra as a function of wavelength of zwitterionic form for RhB dye solution at concentration (10^{-3}) M.

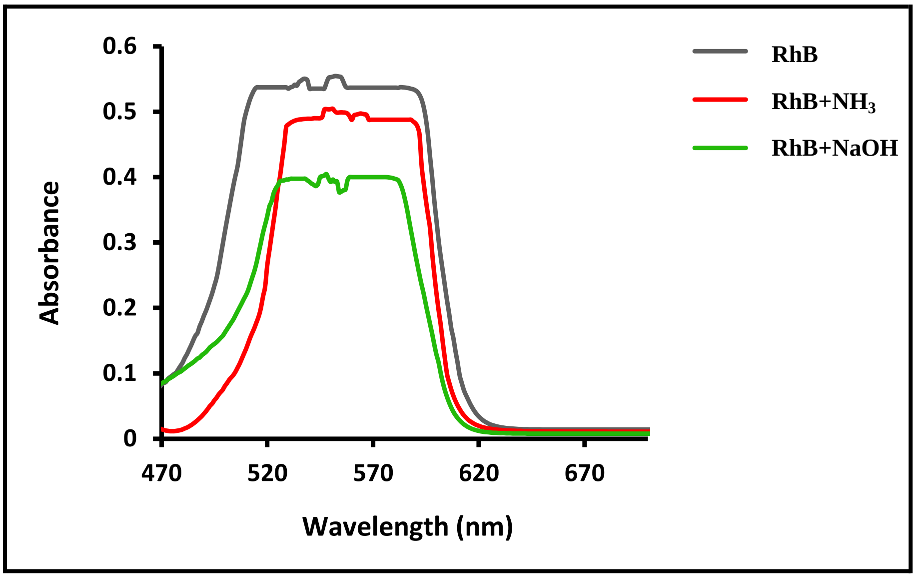


Figure (4.6): Absorbance spectra as a function of wavelength of zwitterionic form for RhB dye solution at concentration (10^{-4}) M.

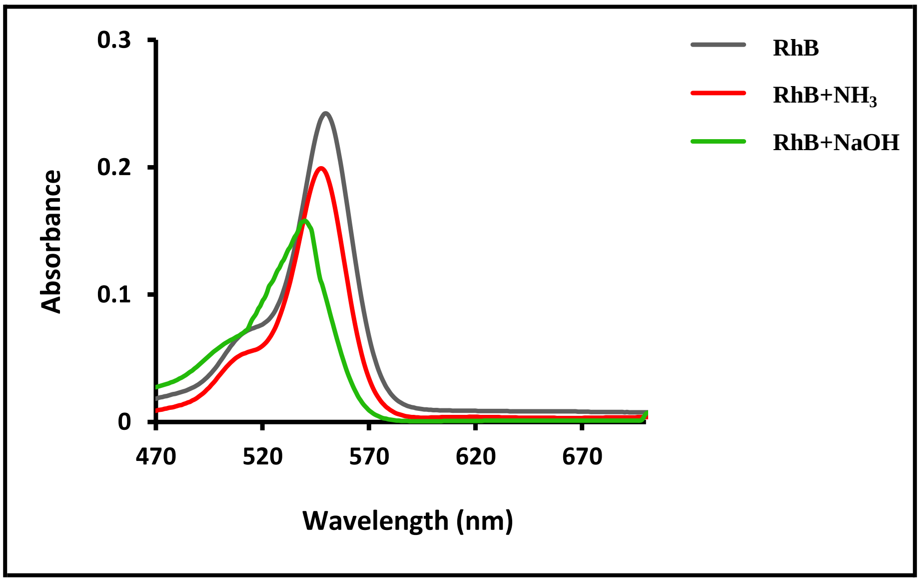


Figure (4.7): Absorbance spectra as a function of wavelength of zwitterionic form for RhB dye solution at concentration (10^{-5}) M.

The blue shift (hypsochromic shift) in the absorbance spectra of zwitterion will be the sum of contributions from each type of interactions : the first interaction is the formation of a hydrogen bond between the solvent and the nitrogen with a lone-pair of electrons. As a consequence, the resonance of the positive charge of the π electron of the chromophore is restricted and a blue shift of the spectrum is expected while the second interaction an electrostatic interaction between the electron donating part of the solvents and the positively charged nitrogen. The resonance of this charge is thereby decreased and therefore a spectral shift to higher energies is expected as well as third interaction between the solvent and the coo- group in the zwitterion form. This interaction influences the effect produced by the (coo-) group on the chromophore through the ninth carbon atom of the xanthene ring [21]. The other structural factor is electrostatic repulsion between negative oxygen atom of carboxyphenyl group and xanthene π electron cloud. This interaction interrupts π electron conjugation of xanthene ring and results in a blue shift of absorbance spectrum [128].

It shows simply from the previous figures that decreasing pH leading to increase of the Absorbance, were the absorbance of cationic form is larger than the pure RhB dye and zwitterionic form respectively, as suggested in the literature [22]. This can be interpreted according to the Bronsted definition, which states that an acid is a hydrogen ion donor. Since HCl is strong acid so the reaction result in complete hydrogen ion transfer into the acidic RhB dye, so the pH will decrease and the absorbance will increase. While in weak acid (CH_3COOH) as complete hydrogen ion transfer does not occur, and therefore its absorbance will be smaller than that of HCl acid. As for the base, it is a hydrogen ion acceptor (the Bronsted base). NaOH is a strong base, so its accepts all hydrogen ions from the acidic RhB dye, so the PH value increases and the absorbance decreases, but in the weak base (NH_3) partial acceptance of hydrogen ions will occur, and therefore its absorption will be less than that of NaOH base [31].

4.2.3 Absorption coefficient

The study of absorption coefficient spectrum of the material provide valuable information about the energy band structure of the material. it is possible to know the nature of electronic transfers that was directly or indirectly by the absorption coefficient values [127]. The linear absorption coefficient (α) is studied by using the absorption data according to equation (2-11). The absorption coefficient spectra as a functions of wavelength of pure RhB dye solution for various concentrations is shown in the figure (4.8).

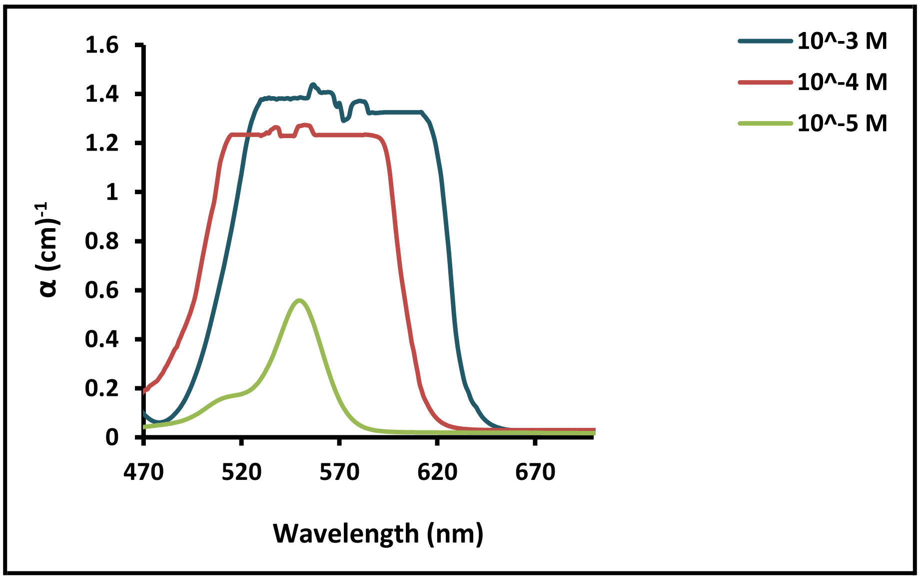


Figure (4.8): Absorption coefficient as a function of wavelength of pure RhB dye solution at different concentrations.

It shows simply different for the peak of the absorption coefficient increases with increasing the concentration because the increase of the number of the absorbing molecules of light, where, the absorption coefficient is directly proportional to the absorbance according to Lambert-Beer law [108]. The absorption coefficient spectra as a functions of wavelength of cationic form for RhB dye solution are shown in the figures (4.9-4.11).

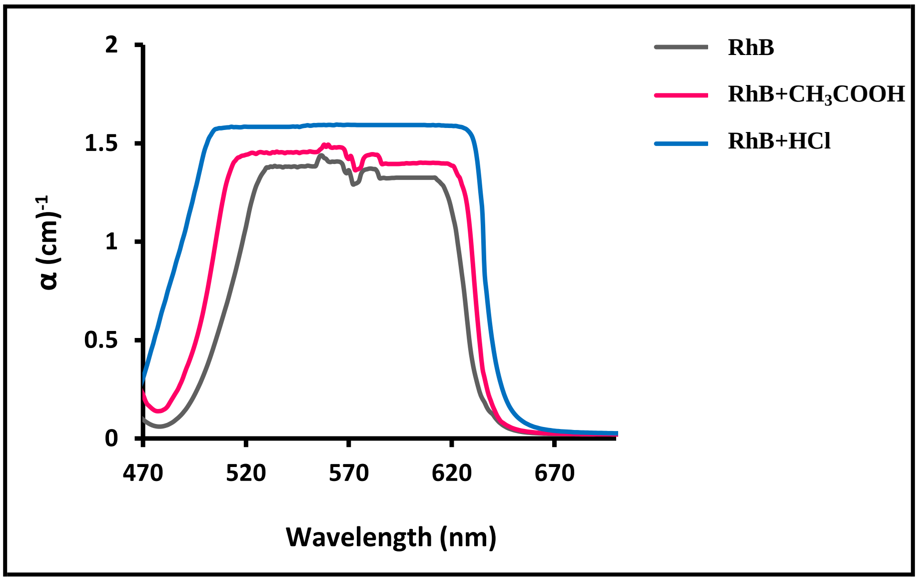


Figure (4.9): Absorption coefficient as a function of wavelength of cationic form for RhB dye solution at concentration (10^{-3}) M.

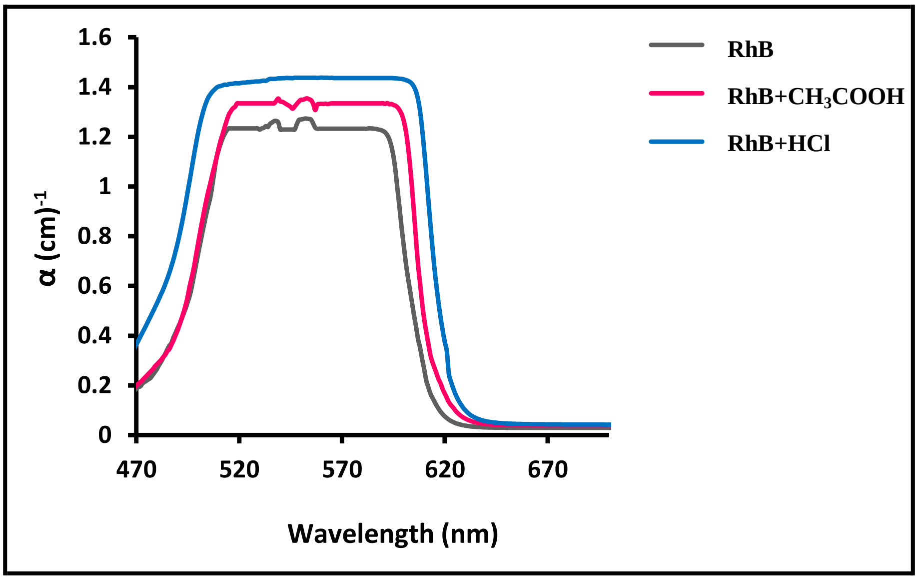


Figure (4.10): Absorption coefficient as a function of wavelength of cationic form for RhB dye solution at concentration (10^{-4}) M.

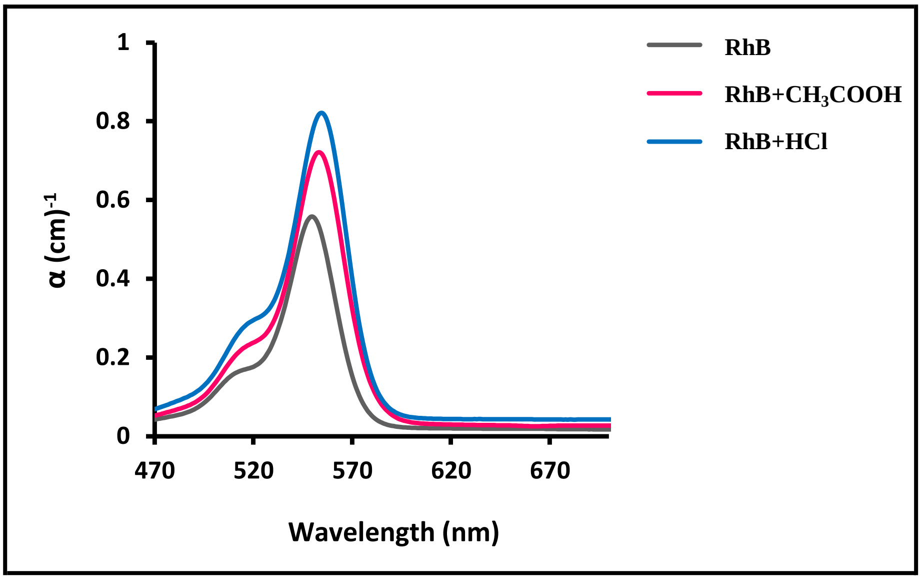


Figure (4.11): Absorption coefficient as a function of wavelength of cationic form for RhB dye solution at concentration (10^{-5}) M.

The absorption coefficient spectra as a functions of wavelength of zwitterionic form for RhB dye solution are shown in the figures (4.12-4.14).

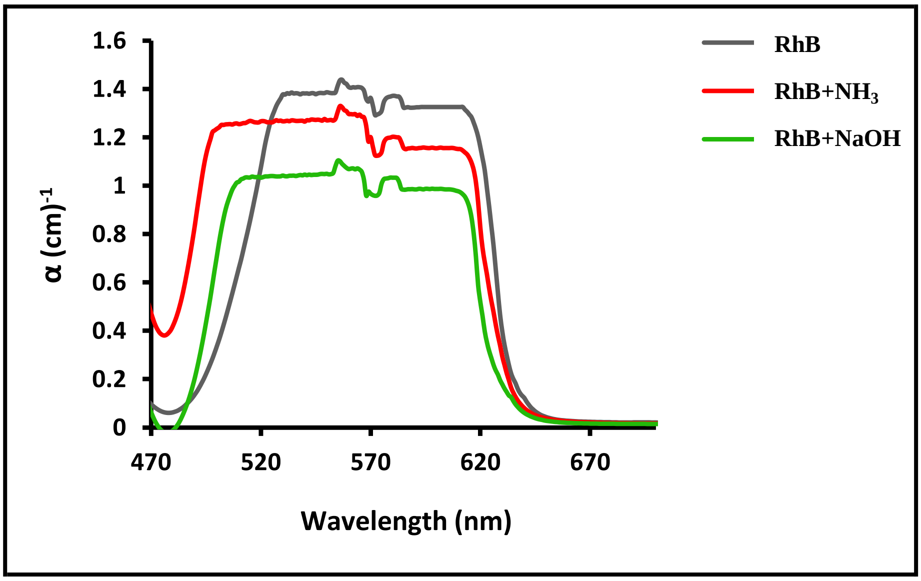


Figure (4.12): Absorption coefficient as a function of wavelength of zwitterionic form for RhB dye solution at concentration (10^{-3}) M.

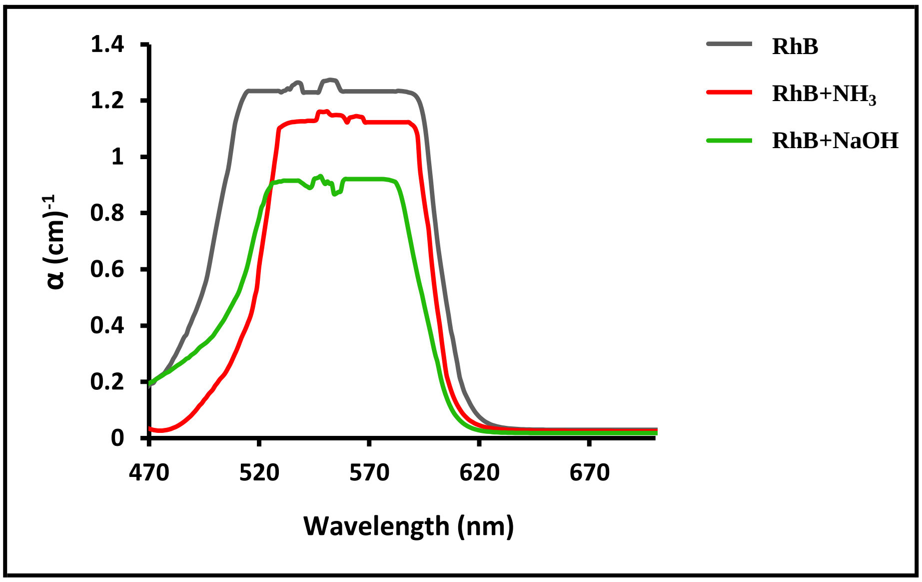


Figure (4.13): Absorption coefficient as a function of wavelength of zwitterionic form for RhB dye solution at concentration (10^{-4}) M.

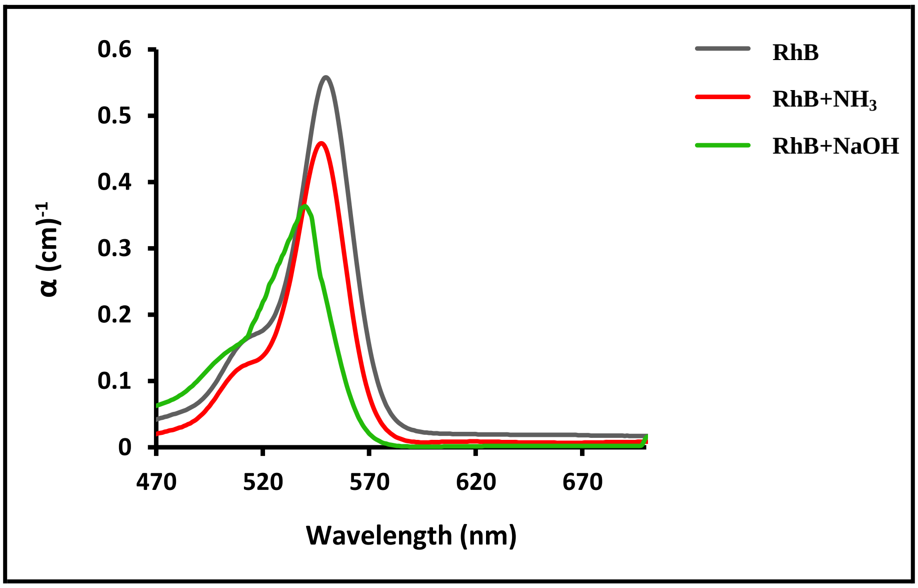


Figure (4.14): Absorption coefficient as a function of wavelength of zwitterionic form for RhB dye solution at concentration (10^{-5}) M.

It is clear from the figures of RhB dye solution before and after addition that the absorption coefficient behaves in a similar to the behavior of the absorption spectrum, this is due to the nature of the relationship between them [134].

4.2.4 Optical energy gap

The estimation of optical energy gap is important to build up the electronic band structure of the laser dye [5]. The optical energy gap of RhB dye solution before and after addition was calculated from the equation (2-17). The figure (4.15) illustrate the case of the pure RhB dye solution for three concentrations, by drawing a relationship between $(\alpha h\upsilon)^{1/2}$ and incident photon energy (hυ) and then draws the straight part to cut axis point (X) of photon energy at the point where $((\alpha h\upsilon)^{1/2}=0)$ which represents the value of the optical energy gap for allowed indirect transitions at the concentrations under the study.

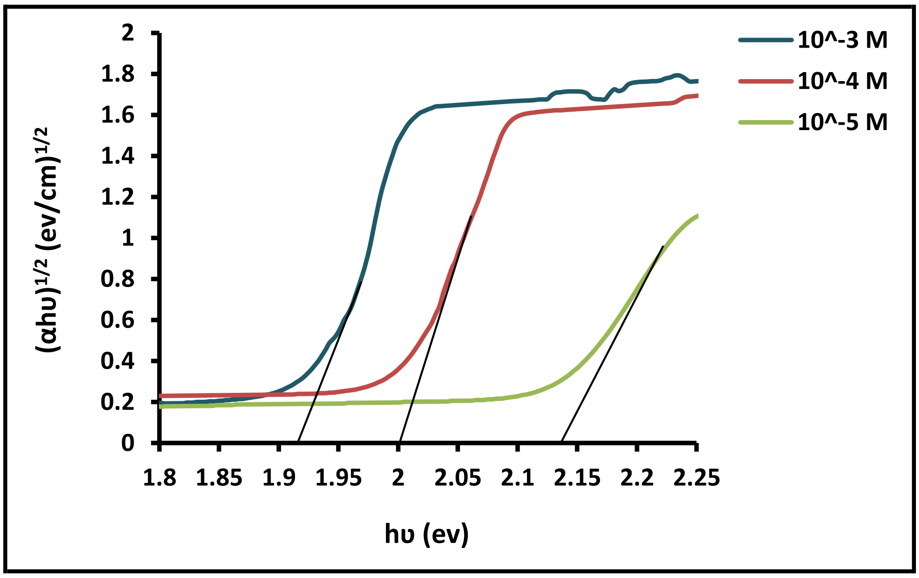


Figure (4.15): The variation of the $(\alpha h\nu)^{1/2}$ with incident photon energy for allowed indirect transition of pure RhB dye solution at different concentrations.

It can be observe from this figure that the energy gap is decrease with the increasing concentration of pure RhB dye solution. The energy gap of the samples decreases with increased concentration of the dye, this due to the creation new levels in energy gap [108,135].

The ground state of the zwitterionic form of the dye has greater solvent stabilization than the ground state of the cationic form, so the energy gap for zwitterionic form would be higher [8], as shown in the figures (4.16 - 4.21).

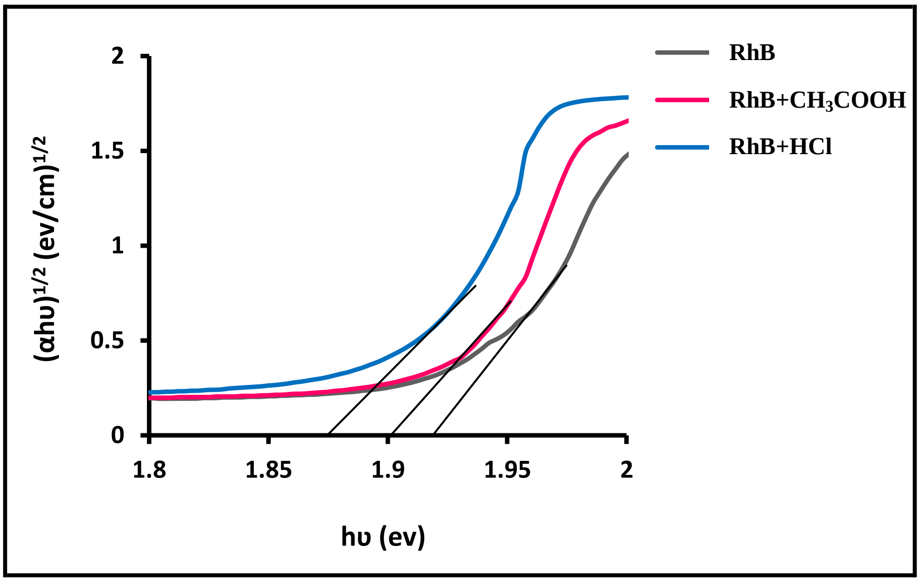


Figure (4.16): The variation of the $(\alpha h\nu)^{1/2}$ with incident photon energy for allowed indirect transition of cationic form of RhB dye solution at concentration (10^{-3}) M.

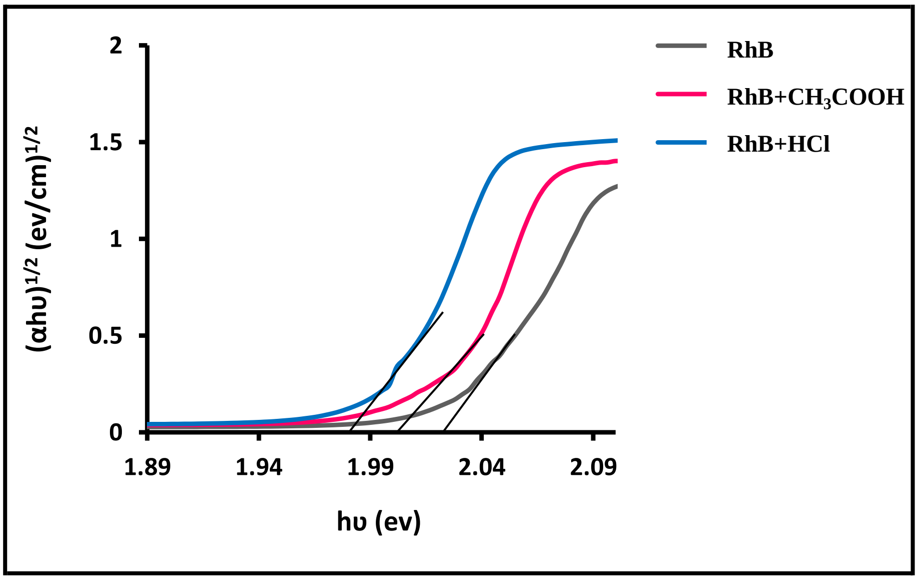


Figure (4.17): The variation of the $(\alpha h\nu)^{1/2}$ with incident photon energy for allowed indirect transition of cationic form of RhB dye solution at concentration (10^{-4}) M.

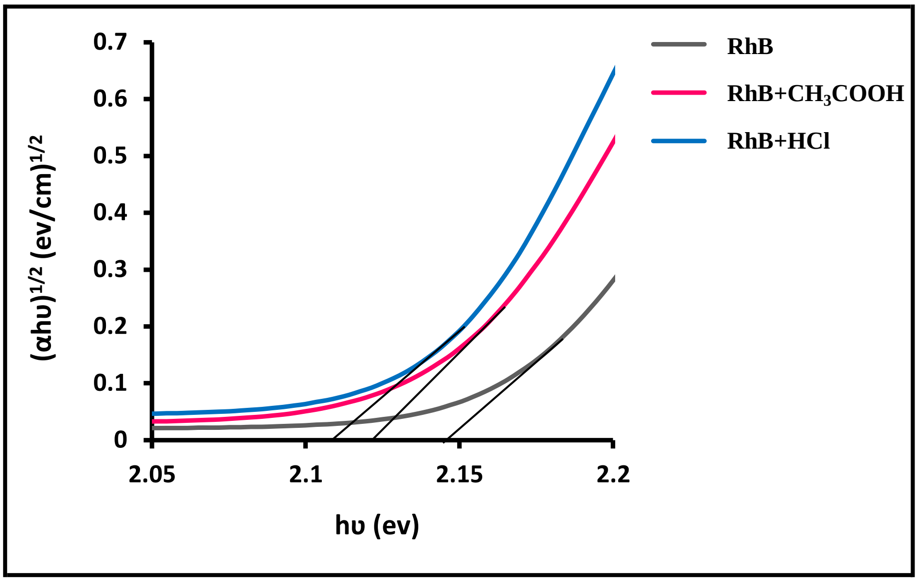


Figure (4.18): The variation of the $(\alpha h\nu)^{1/2}$ with incident photon energy for allowed indirect transition of cationic form of RhB dye solution at concentration (10^{-5}) M.

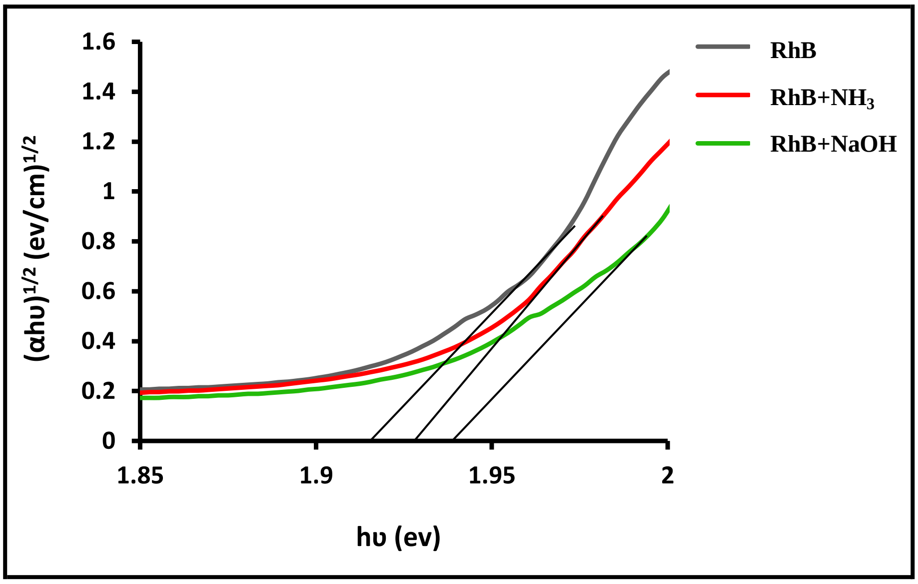


Figure (4.19): The variation of the $(\alpha h\nu)^{1/2}$ with incident photon energy for allowed indirect transition of zwitterionic form of RhB dye solution at concentration (10^{-3}) M.

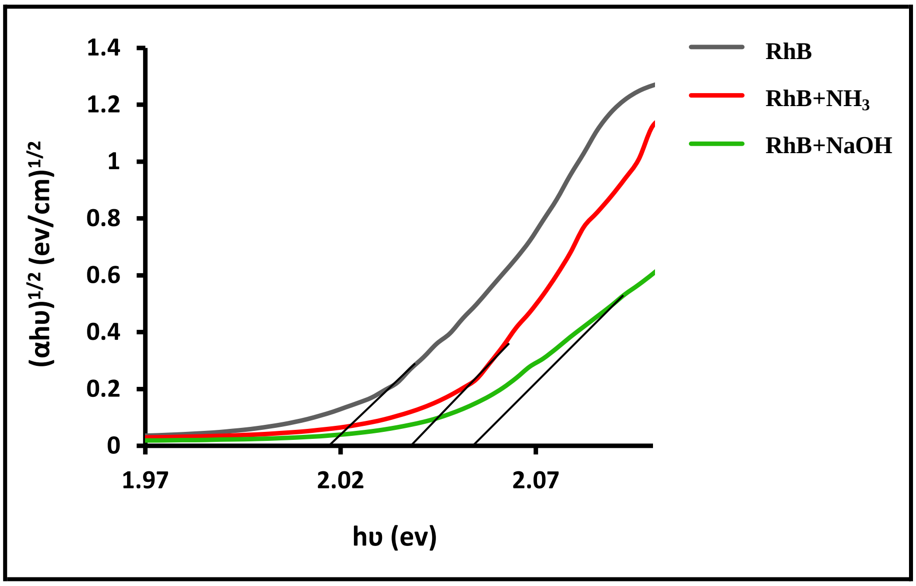


Figure (4.20): The variation of the $(\alpha h\nu)^{1/2}$ with incident photon energy for allowed indirect transition of zwitterionic form of RhB dye solution at concentration (10^{-4}) M.

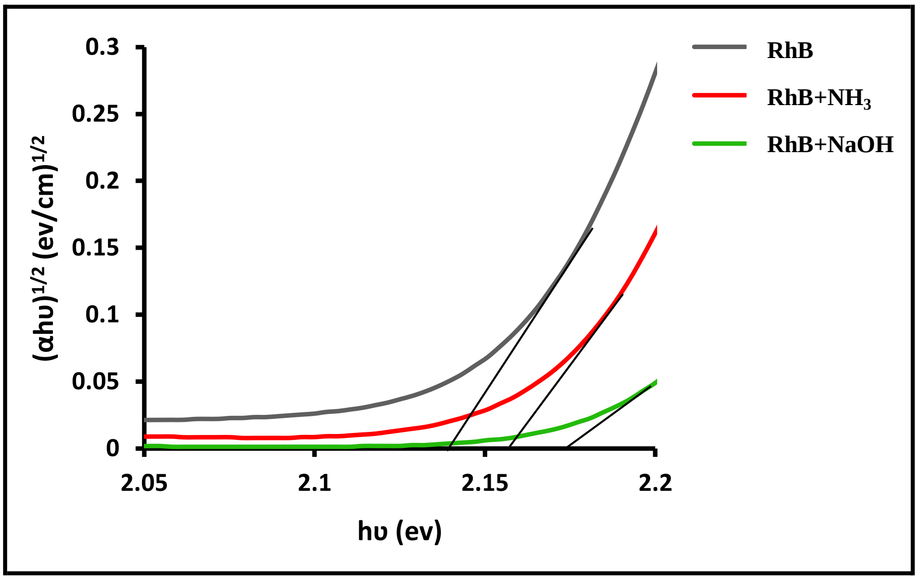


Figure (4.21): The variation of the $(\alpha h\nu)^{1/2}$ with incident photon energy for allowed indirect transition of zwitterionic form of RhB dye solution at concentration (10^{-5}) M.

The following figures (4.22-4.28) illustrate the forbidden energy gap of the RhB dye solutions before and after addition for three concentrations, by drawing a relation between (αhυ) and incident photon energy (hυ) and draws the straight part to cut axis point (X) of photon energy at the point where ($(\alpha h\upsilon)^{1/3}$ = 0), which represents the value of the optical energy gap for forbidden indirect transitions at the concentrations under the study.

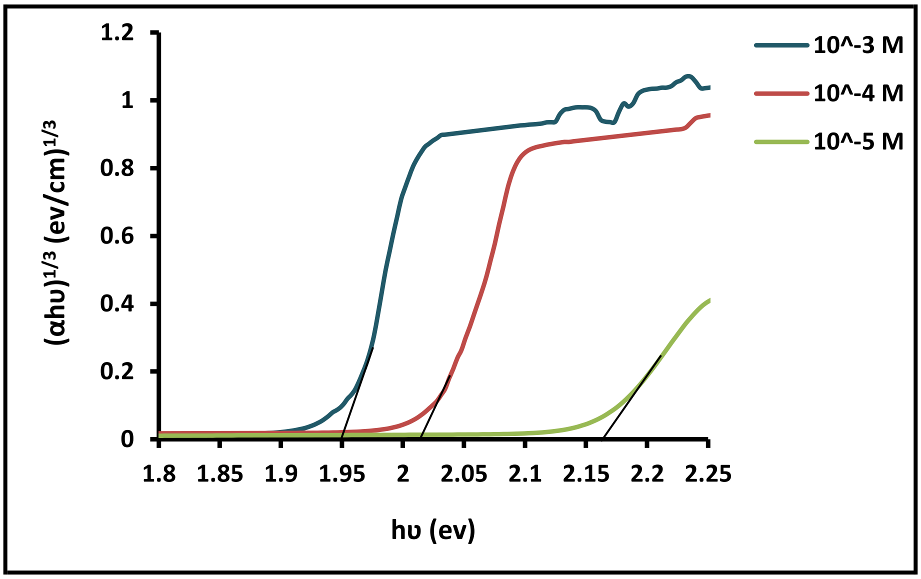


Figure (4.22): The variation of the $(\alpha h\nu)^{1/3}$ with incident photon energy for forbidden indirect transition of pure RhB dye solution at different concentrations.

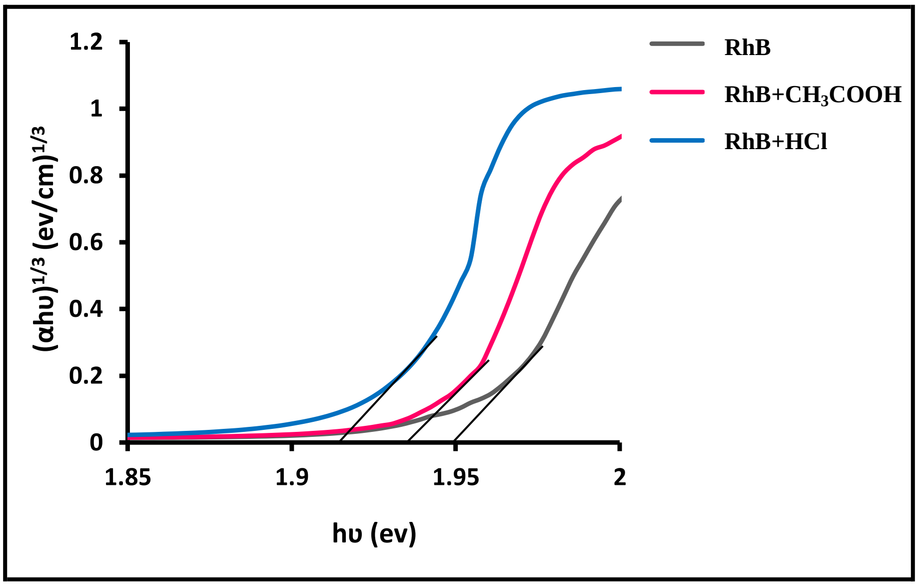


Figure (4.23): The variation of the $(\alpha h\nu)^{1/3}$ with incident photon energy for forbidden indirect transition of cationic form of RhB dye solution at concentration (10^{-3}) M.

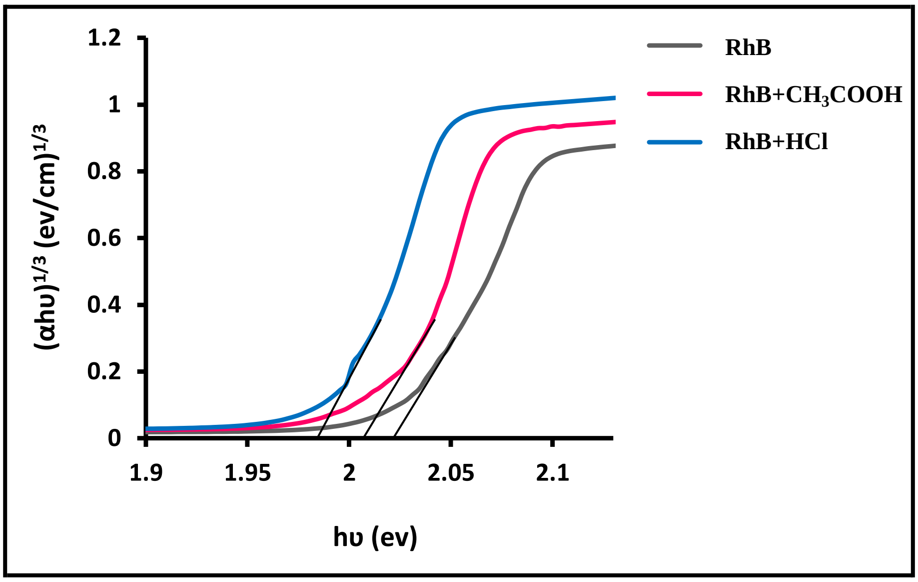


Figure (4.24): The variation of the $(\alpha h\nu)^{1/3}$ with incident photon energy for forbidden indirect transition of cationic form of RhB dye solution at concentration (10^{-4}) M.

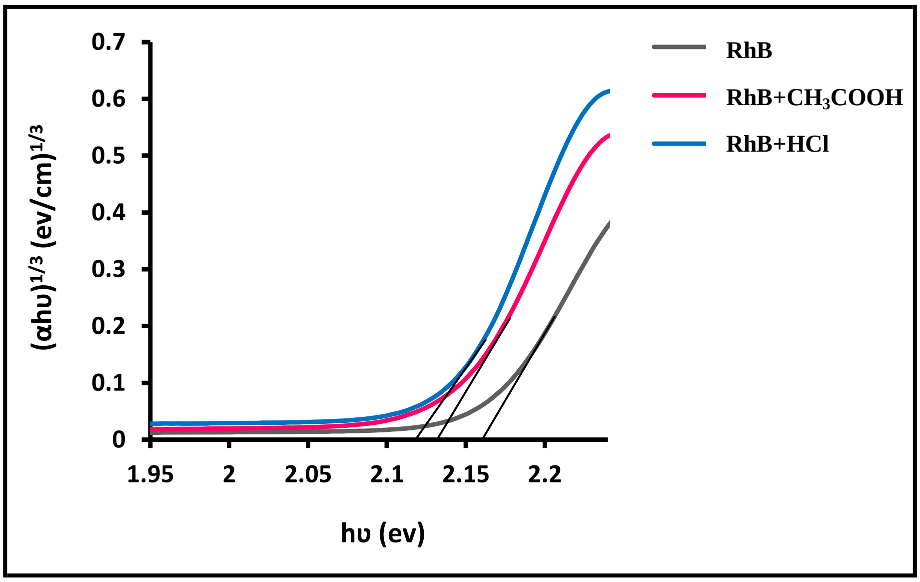


Figure (4.25): The variation of the $(\alpha h\nu)^{1/3}$ with incident photon energy for forbidden indirect transition of cationic form of RhB dye solution at concentration (10^{-5}) M.

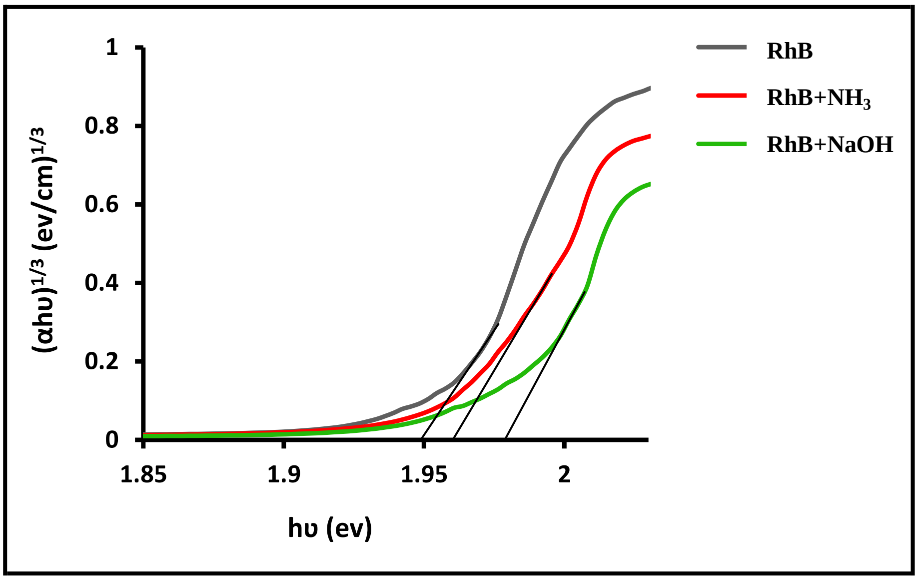


Figure (4.26): The variation of the $(\alpha h\nu)^{1/3}$ with incident photon energy for forbidden indirect transition of zwitterionic form of RhB dye solution at concentration (10^{-3}) M.

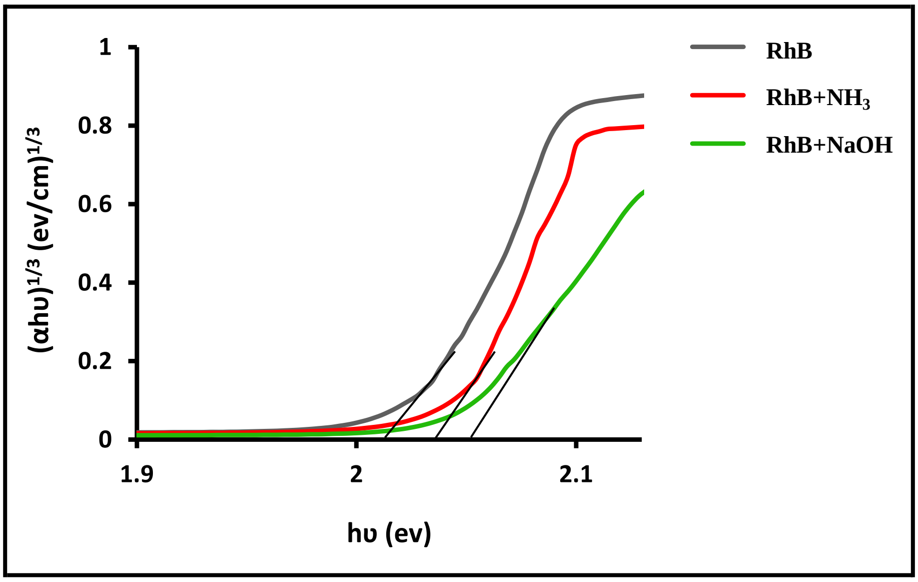


Figure (4.27): The variation of the $(\alpha h\nu)^{1/3}$ with incident photon energy for forbidden indirect transition of zwitterionic form of RhB dye solution at concentration (10^{-4}) M.

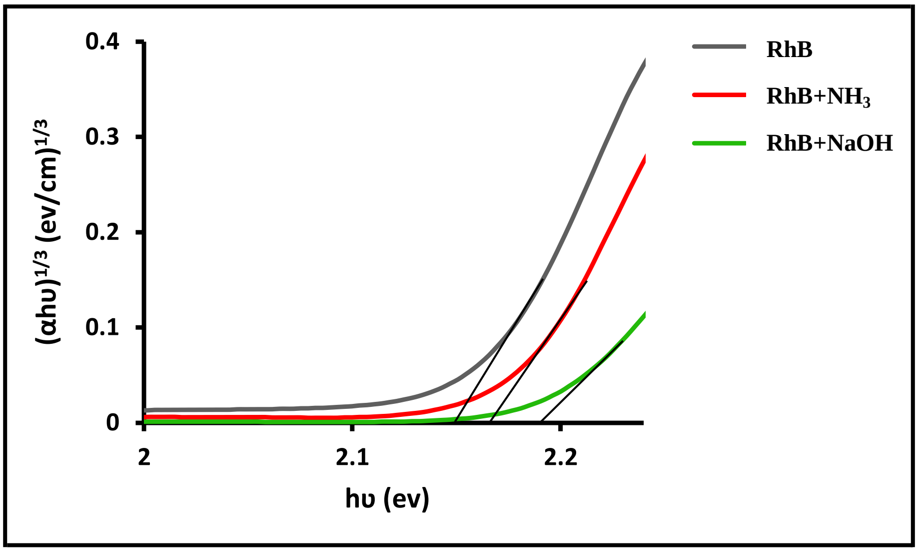


Figure (4.28): The variation of the $(\alpha h\nu)^{1/3}$ with incident photon energy for forbidden indirect transition of zwitterionic form of RhB dye solution at concentration (10^{-5}) M.

4.2.5 Refractive index

Evaluation of the refractive indices of optical materials is considerably important for the applications in optics devices[127]. The index of refraction is useful for optical constants and calculated from the equation (2-13). The figure (4.29) shows the behavior of refractive index of pure RhB dye solution at different concentrations.

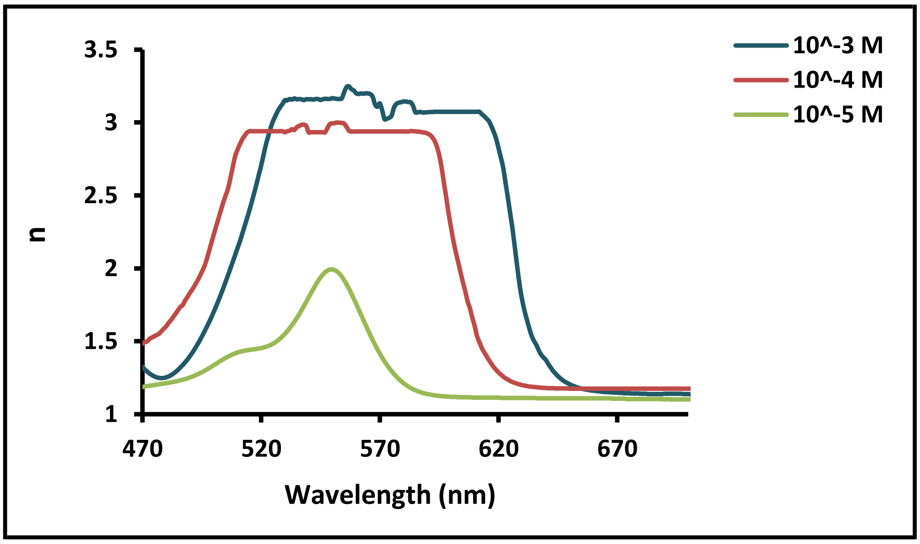


Figure (4.29): Refractive index as a function of wavelength of pure RhB dye solution at different concentrations.

It is observed that, the refractive index varies with a wavelength, and the spectrum peak of the refractive index is increased with increasing the concentration. This is due to the increase the density of the sample with increasing the dye concentration[108].

The refractive index as a function of wavelength of cationic and zwitterionic forms of RhB dye solution at different concentration are shown in the figures (4.30-4.35), respectively.

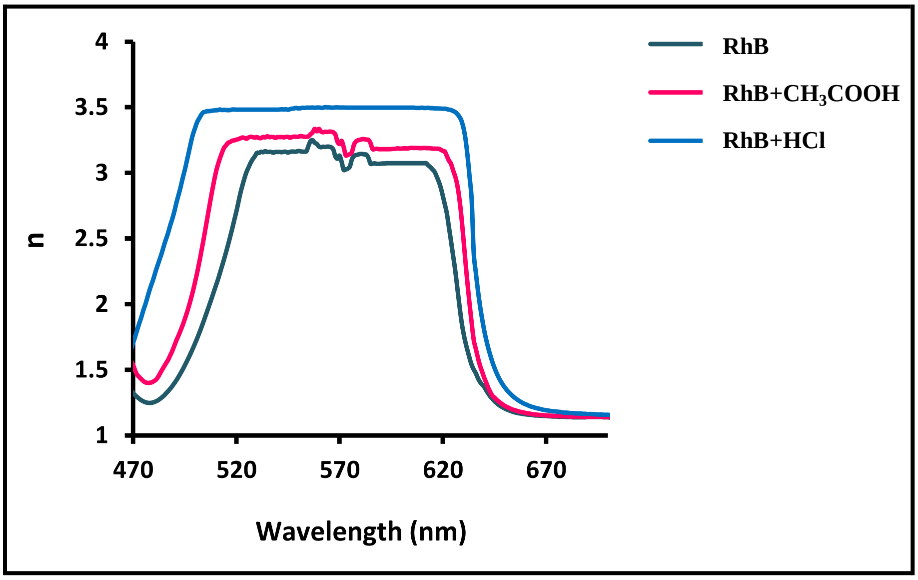


Figure (4.30): Refractive index as a function of wavelength of cationic form for RhB dye solution at concentration (10^{-3}) M.

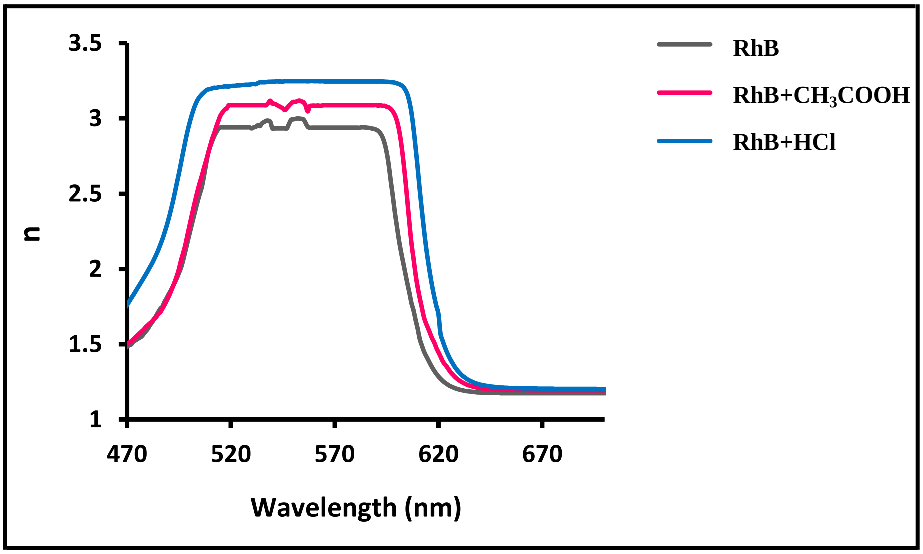


Figure (4.31): Refractive index as a function of wavelength of cationic form for RhB dye solution at concentration (10^{-4}) M.

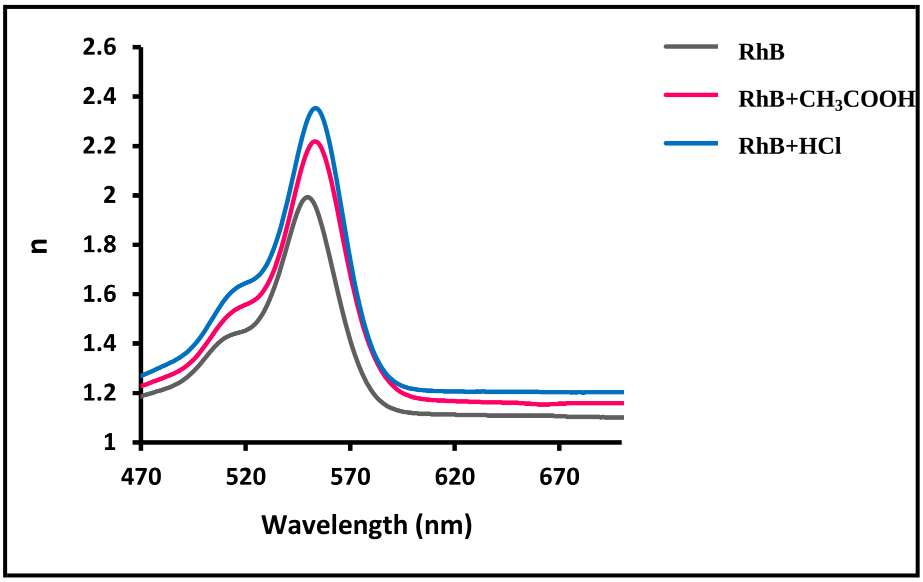


Figure (4.32): Refractive index as a function of wavelength of cationic form for RhB dye solution at concentration (10^{-5} M).

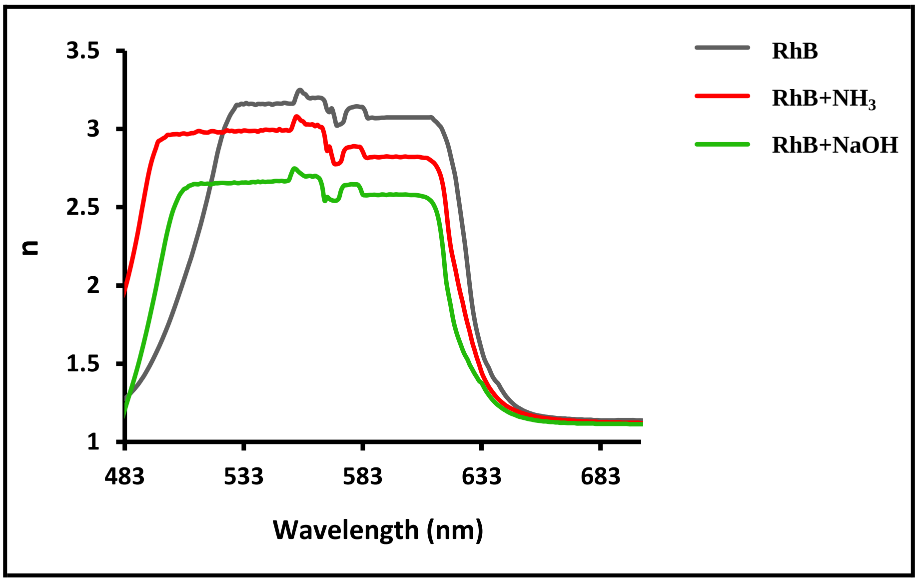


Figure (4.33): Refractive index as a function of wavelength of zwitterionic form for RhB dye solution at concentration (10^{-3}) M.

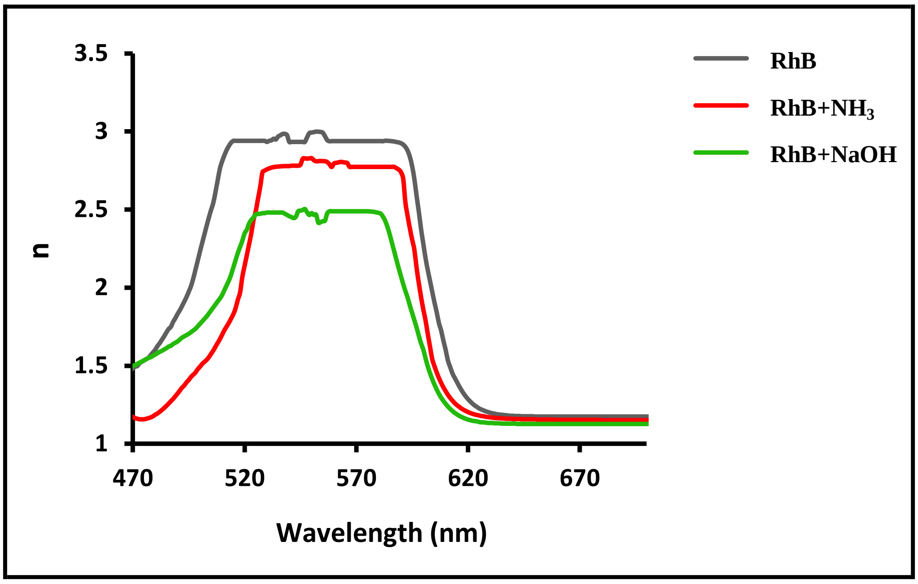


Figure (4.34): Refractive index as a function of wavelength of zwitterionic form for RhB dye solution at concentration (10^{-4}) M.

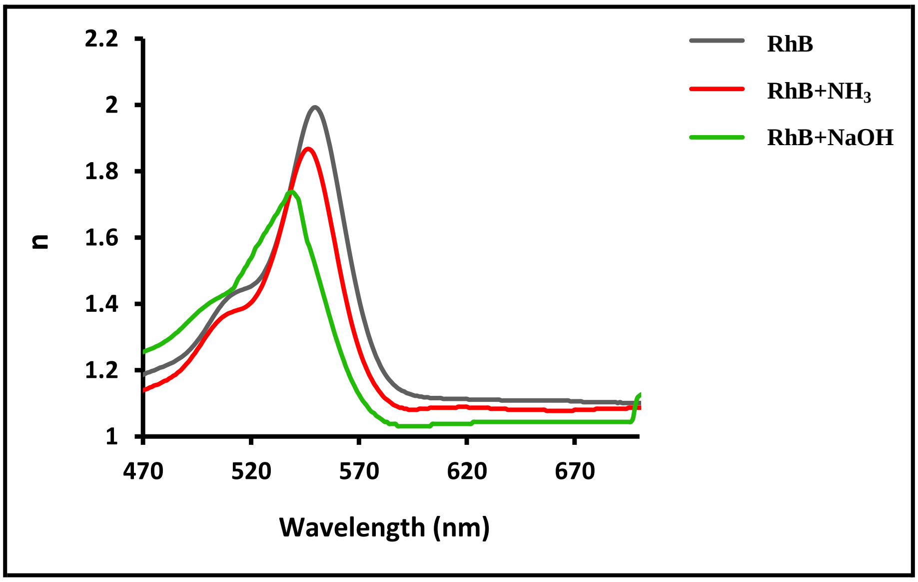


Figure (4.35): Refractive index as a function of wavelength of zwitterionic form for RhB dye solution at concentration (10^{-5}) M.

The refractive index is inversely proportional with optical energy gap [136]. The reduction in optical band gap indicate that there are new levels generated in the energy gap and thus increases in refractive index. Since the energy gap of cationic form is less than zwitterionic form, so the refractive index of the cationic form would be higher.

4.2.6 Extinction coefficient

The extinction coefficient k describes the properties of the material with respect to light of a given wavelength and indicates the absorption changes when the electromagnetic wave propagates through the material [136]. The extinction coefficient (k) has been calculated by using equation (2-14), the extinction coefficient as a function of wavelength of pure RhB dye solution at different concentrations is shown in figure (4.36).

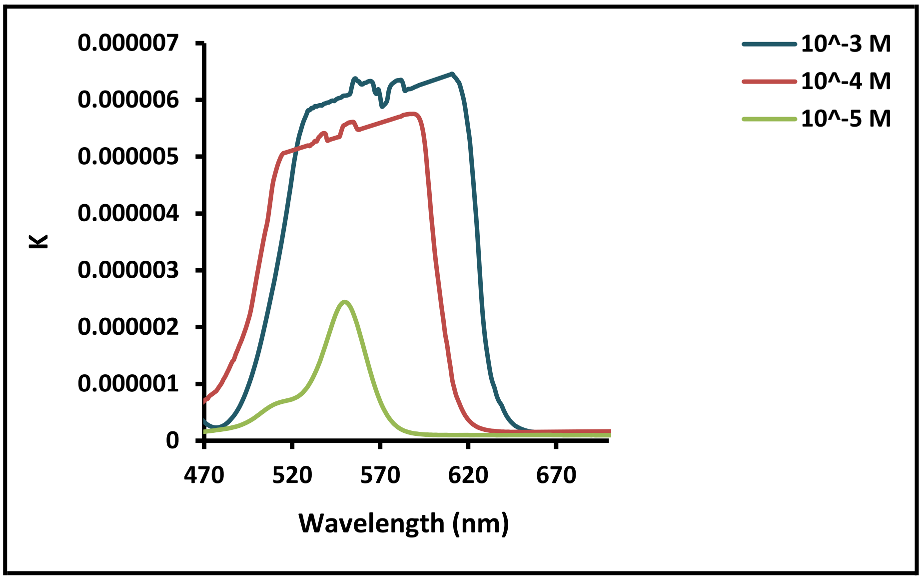


Figure (4.36): Extinction coefficient as a function of wavelength of pure RhB dye solution at different concentrations.

It was observed that the extinction coefficient varies with the light wavelength, and the peak of the extinction coefficient increases with increasing the dye concentration due to the increase the absorption coefficient, where the extinction coefficient depends on the absorption coefficient.

The extinction coefficient as a function of wavelength of cationic and zwitterionic forms of RhB dye solution at different concentration are shown in the figures (4.37-4.42), respectively.

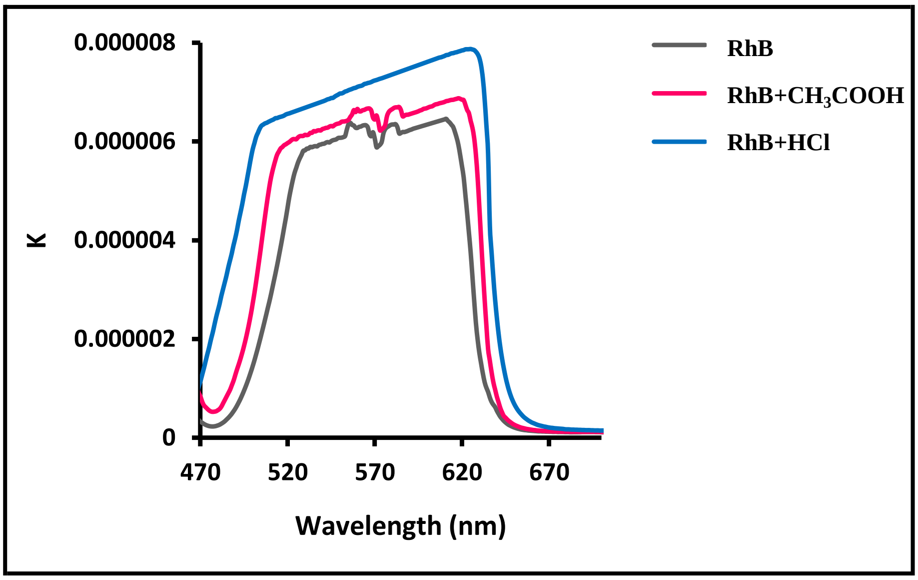


Figure (4.37): Extinction coefficient as a function of wavelength of cationic form for RhB dye solution at concentration (10^{-3} M).

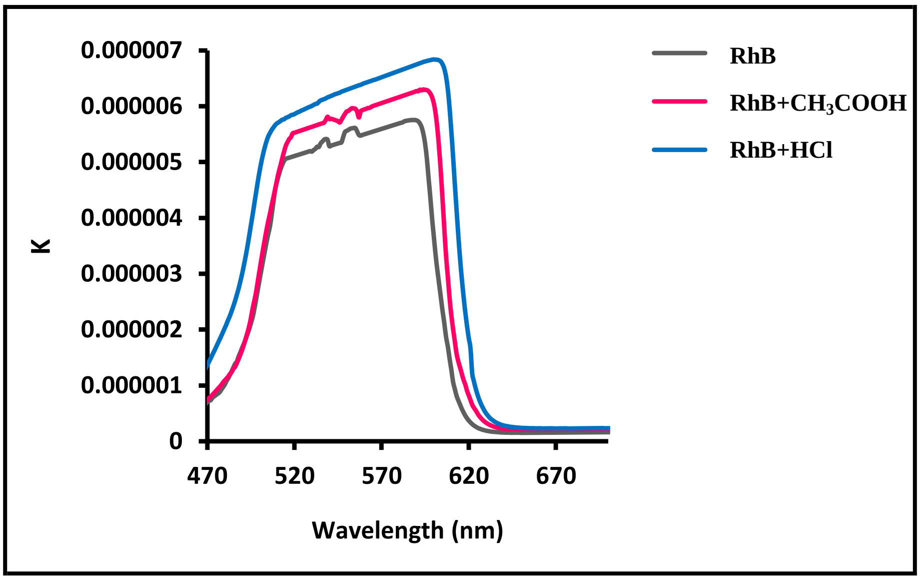


Figure (4.38): Extinction coefficient as a function of wavelength of cationic form for RhB dye solution at concentration (10^{-4} M).

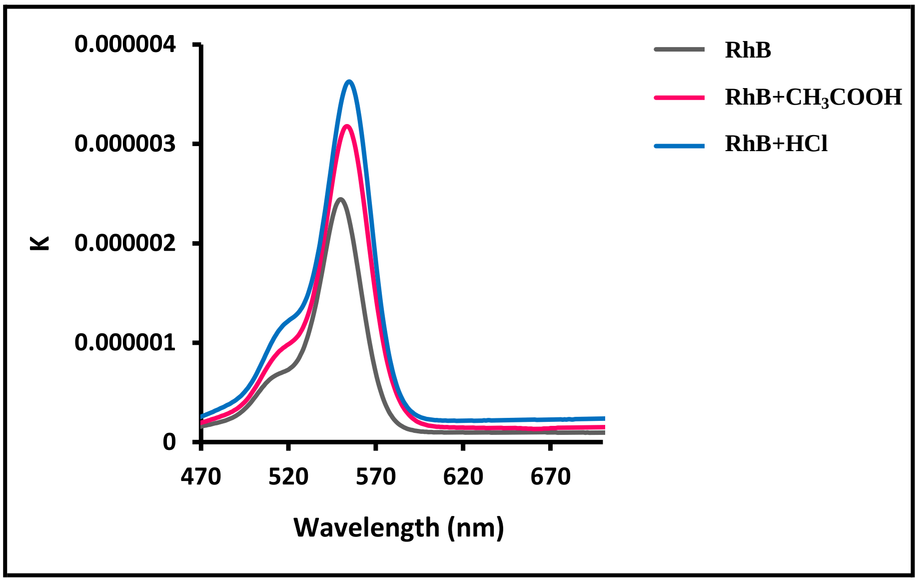


Figure (4.39): Extinction coefficient as a function of wavelength of cationic form for RhB dye solution at concentration (10^{-5} M).

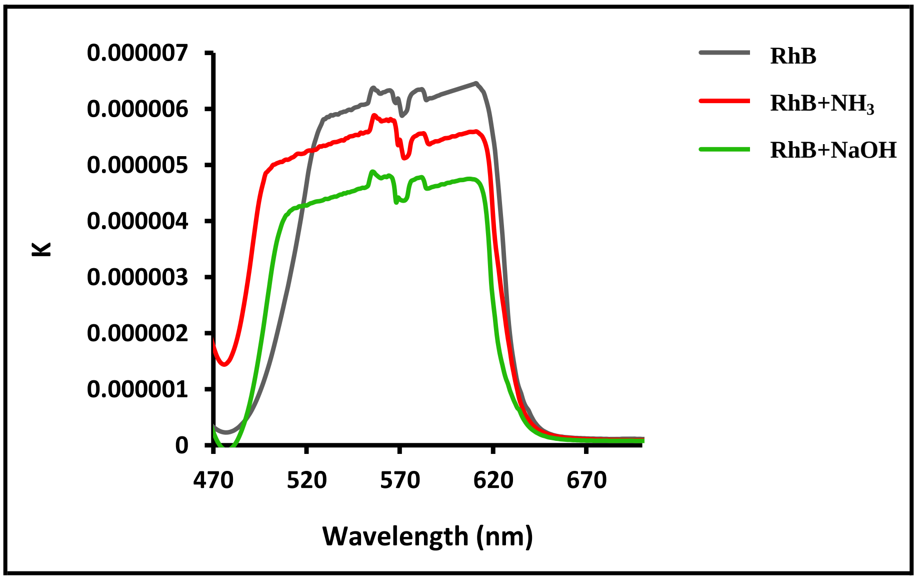


Figure (4.40): Extinction coefficient as a function of wavelength of zwitterionic form for RhB dye solution at concentration (10^{-3} M).

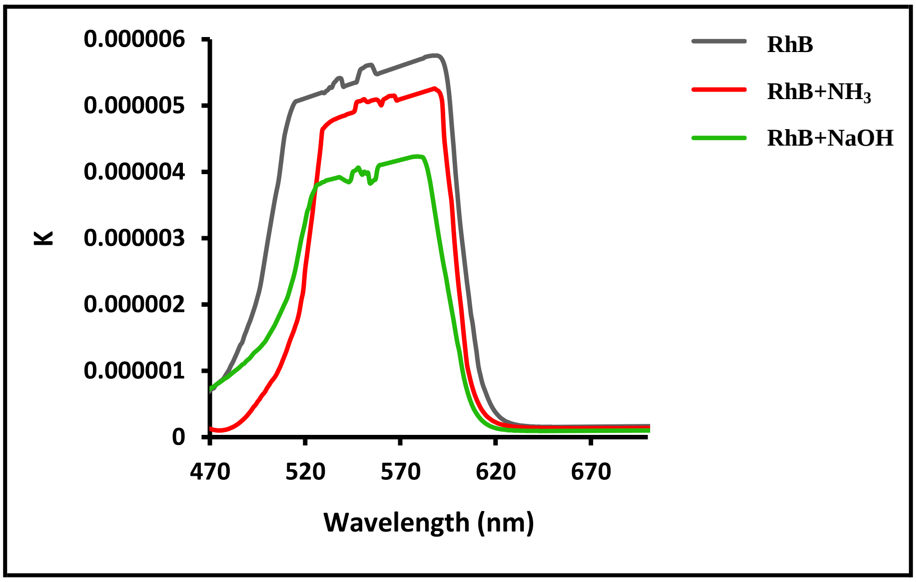


Figure (4.41): Extinction coefficient as a function of wavelength of zwitterionic form for RhB dye solution at concentration (10^{-4} M).

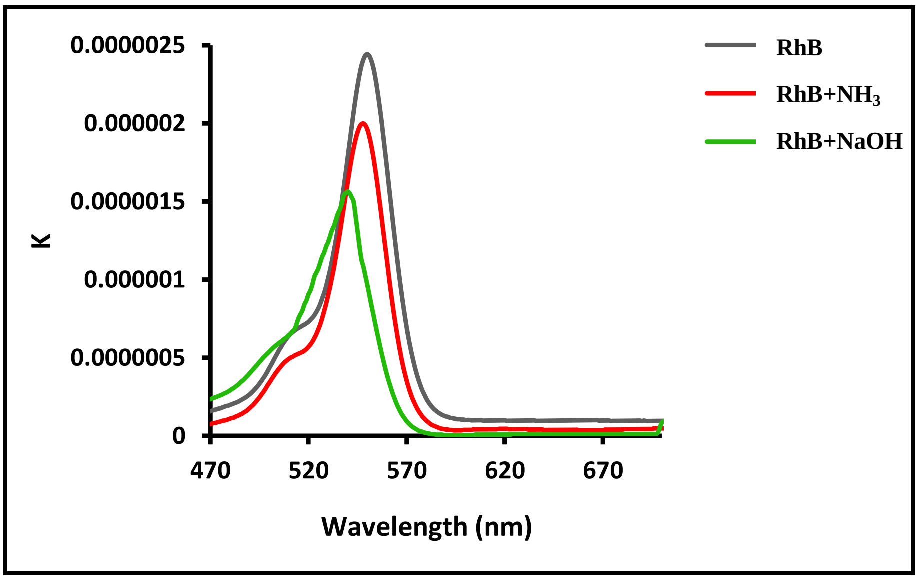


Figure (4.42): Extinction coefficient as a function of wavelength of zwitterionic form for RhB dye solution at concentration (10^{-5} M).

4.2.7 Dielectric constant

The dielectric constant (ε) consists of a real part and an imaginary part, which depend on the frequency of the electromagnetic wave. the real part associated with the term that shows how much it will slow down the speed of light in the material. The imaginary part of the dielectric constant shows how a dielectric absorbs energy from an electric field due to dipole motion. The real part of dielectric constant is related to the dispersion, and the imaginary part represents the dissipative rate of electromagnetic wave propagation in the medium [136].

The real part of the dielectric constant were determined from equation (2-19), The real dielectric constant as a function of wavelength of pure RhB dye solution and cationic form are shown in figures (4.43- 4.46), respectively.

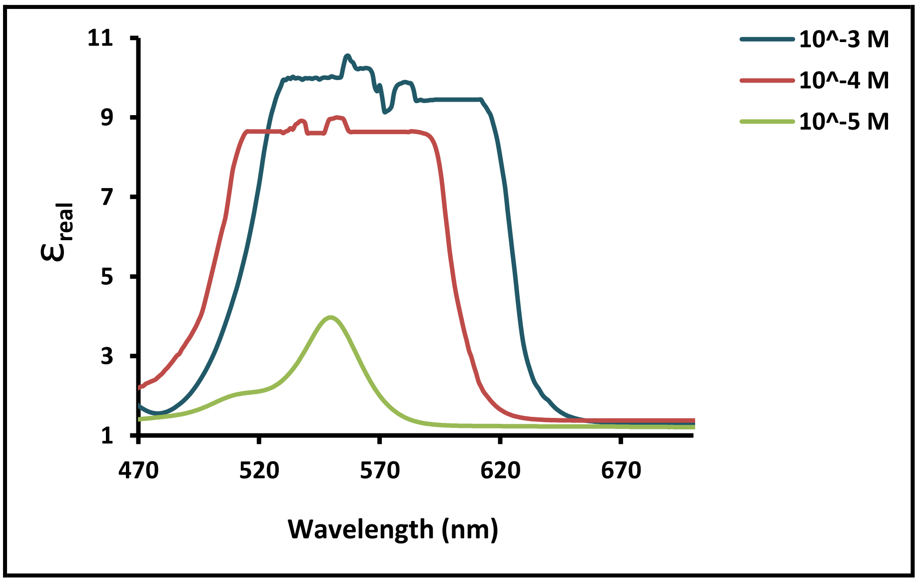


Figure (4.43): Real dielectric constant as a function of wavelength of pure RhB dye solution at different concentrations.

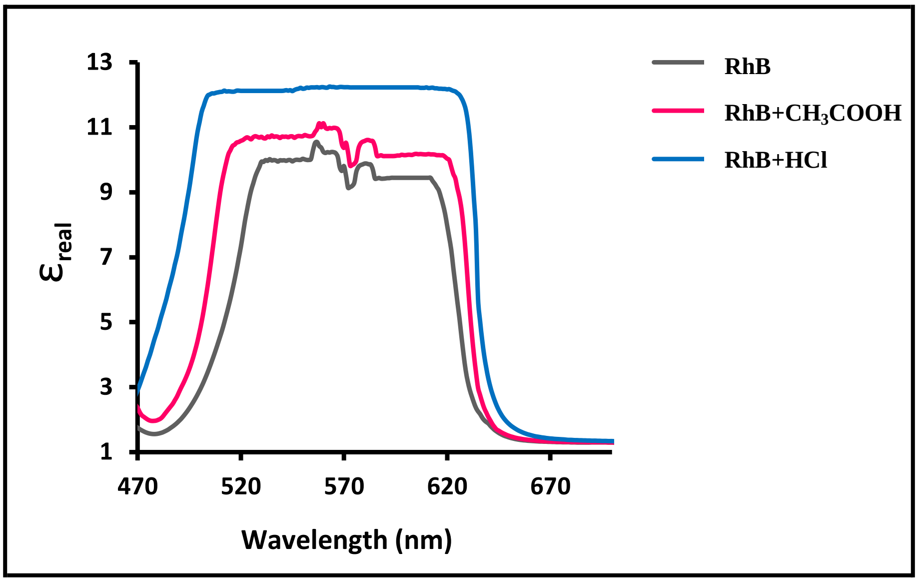


Figure (4.44): Real dielectric constant as a function of wavelength of cationic form for RhB dye solution at concentration (10^{-3}) M.

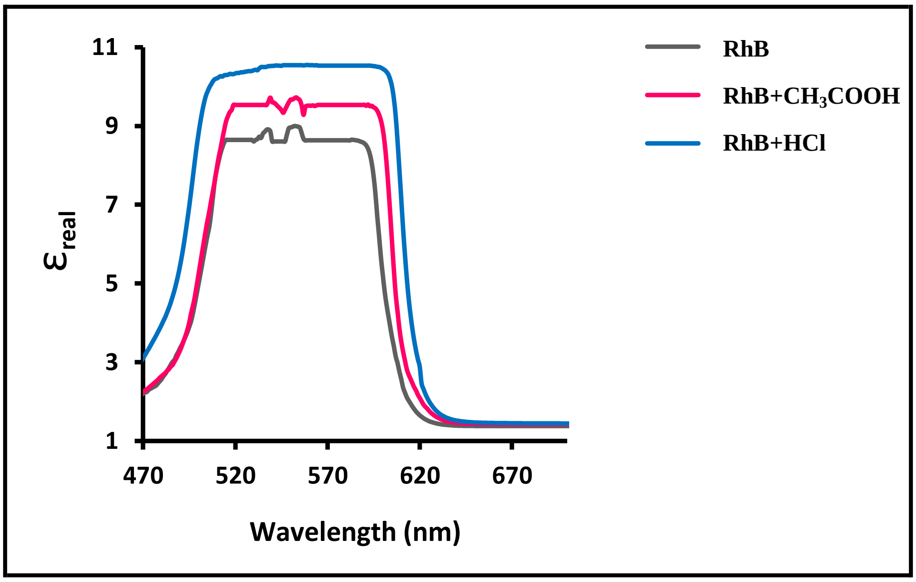


Figure (4.45): Real dielectric constant as a function of wavelength of cationic form for RhB dye solution at concentration (10^{-4}) M.

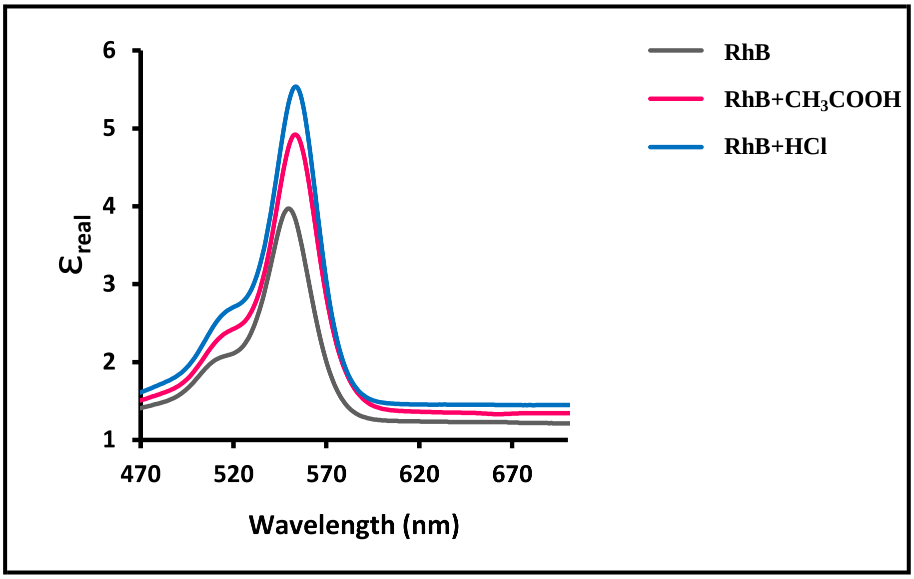


Figure (4.46): Real dielectric constant as a function of wavelength of cationic form for RhB dye solution at concentration (10^{-5}) M.

The imaginary part of the dielectric constant were determined from equation (2-20), The relationship of imaginary dielectric constant with wavelength of pure RhB dye solution and cationic form are shown in figures (4.47- 4.50), respectively.

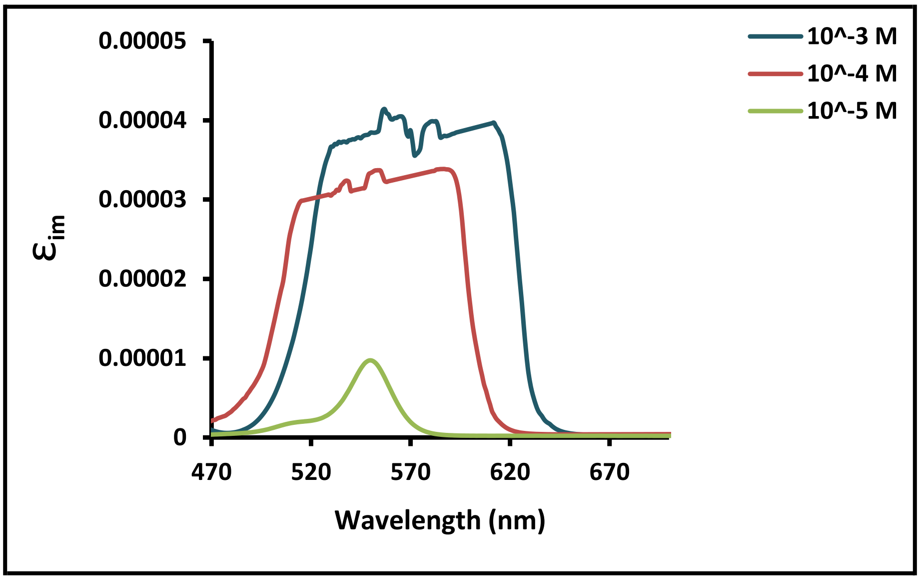


Figure (4.47): Imaginary dielectric constant as a function of wavelength of pure RhB dye solution at different concentrations.

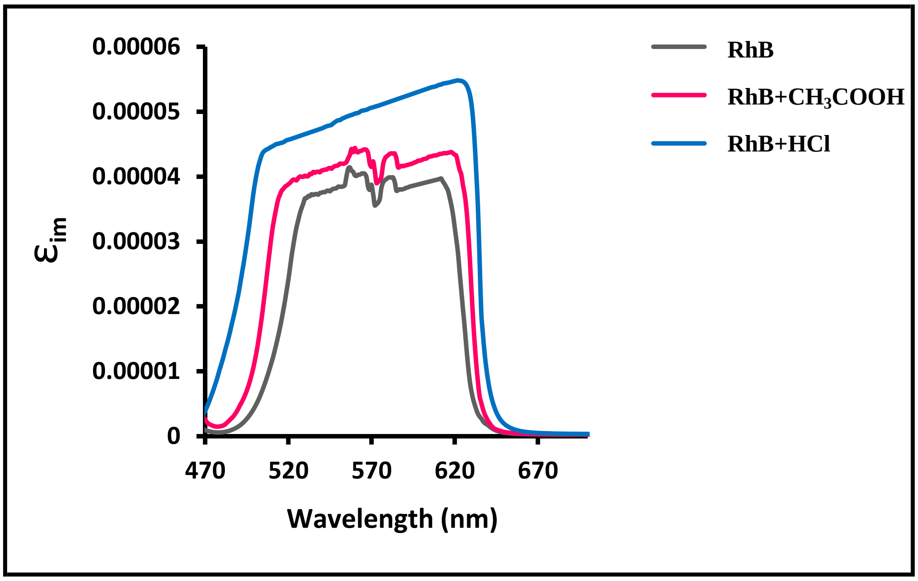


Figure (4.48): Imaginary dielectric constant as a function of wavelength of cationic form for RhB dye solution at concentration (10^{-3}) M.

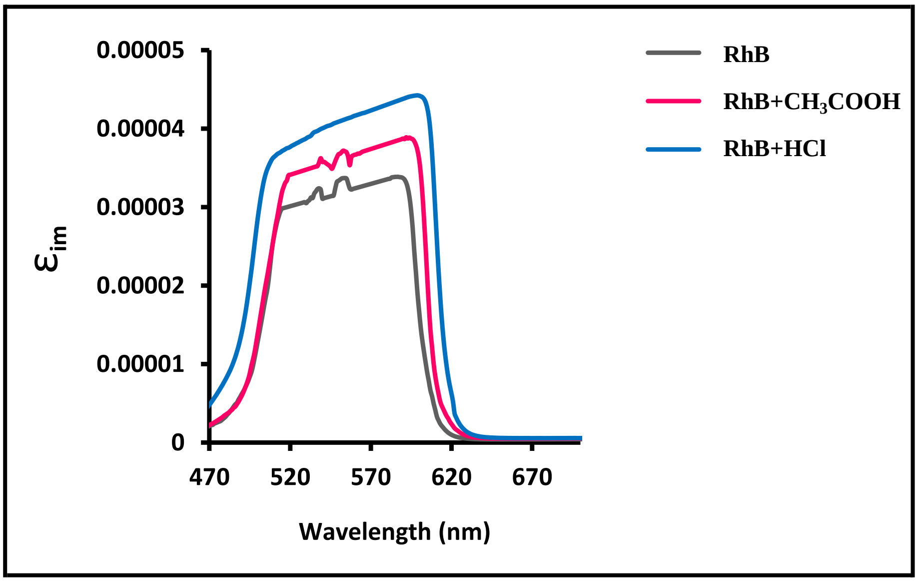


Figure (4.49): Imaginary dielectric constant as a function of wavelength of cationic form for RhB dye solution at concentration (10^{-4}) M.

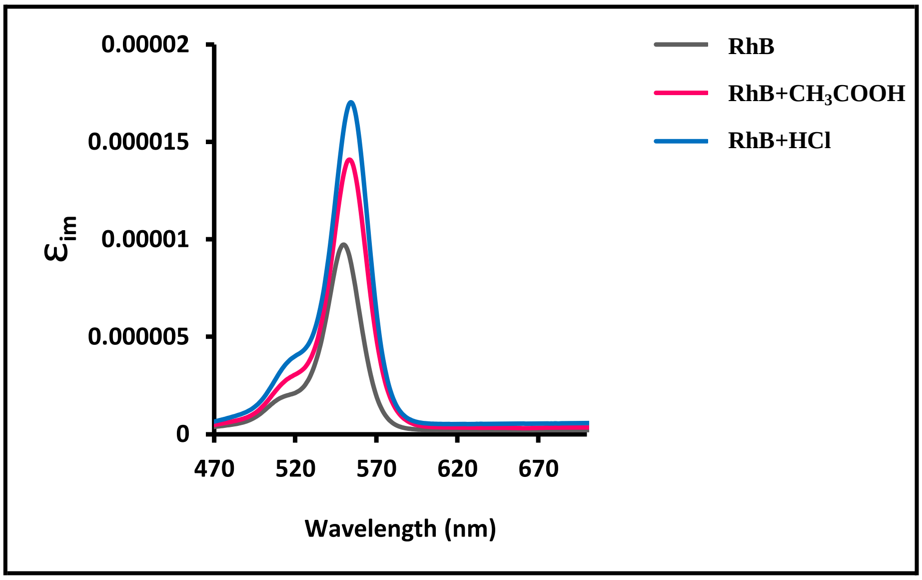


Figure (4.50): Imaginary dielectric constant as a function of wavelength of cationic form for RhB dye solution at concentration (10^{-5}) M.

The relation of real and imaginary dielectric constant as a function of wavelength for zwitterionic form are shown in the figures (4.51- 4.56), respectively.

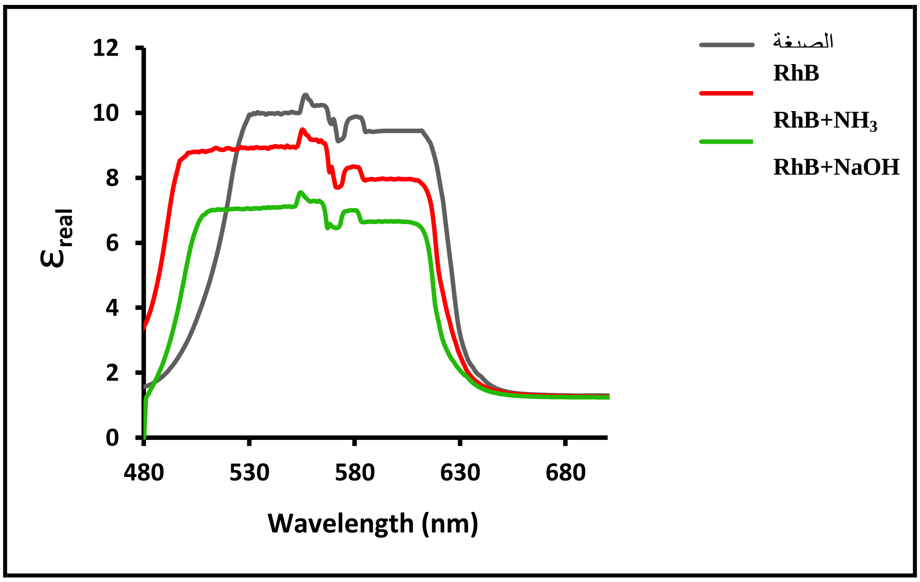


Figure (4.51): Real dielectric constant as a function of wavelength of zwitterionic form for RhB dye solution at concentration (10^{-3}) M.

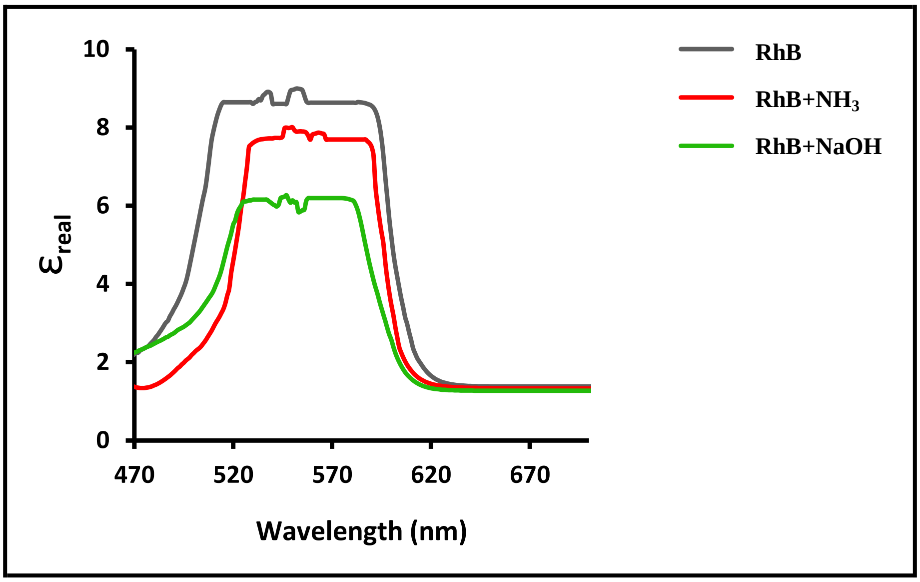


Figure (4.52): Real dielectric constant as a function of wavelength of zwitterionic form for RhB dye solution at concentration (10^{-4}) M.

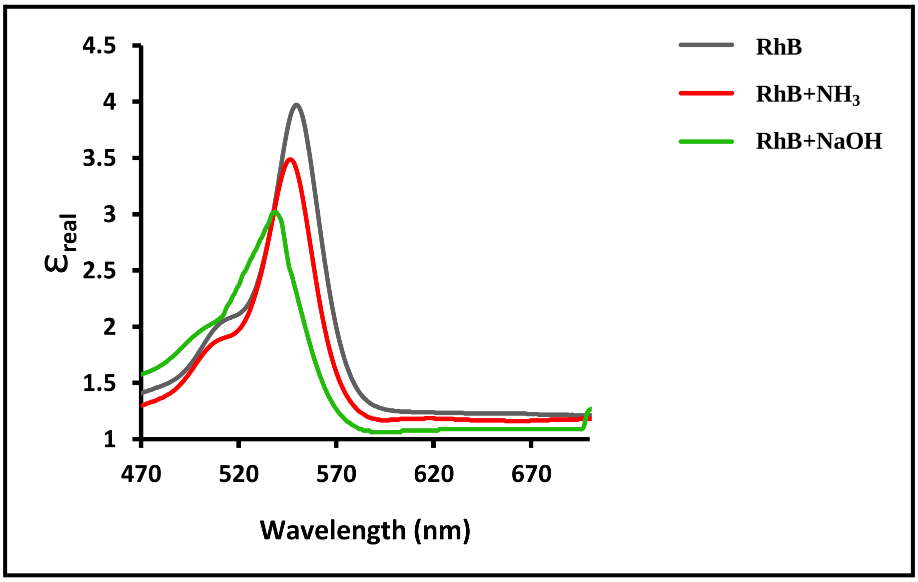


Figure (4.53): Real dielectric constant as a function of wavelength of zwitterionic form for RhB dye solution at concentration (10^{-5}) M.

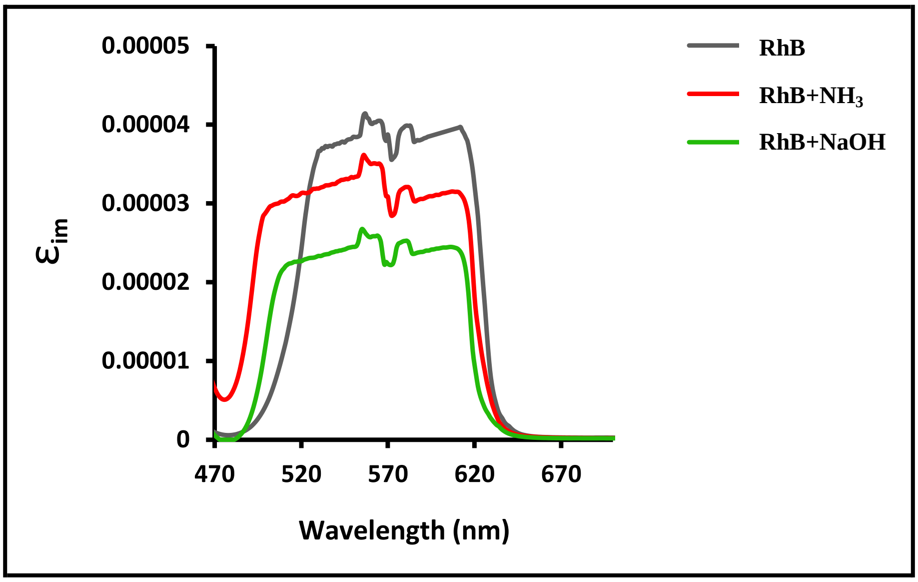


Figure (4.54): Imaginary dielectric constant as a function of wavelength of zwitterionic form for RhB dye solution at concentration (10^{-3}) M.

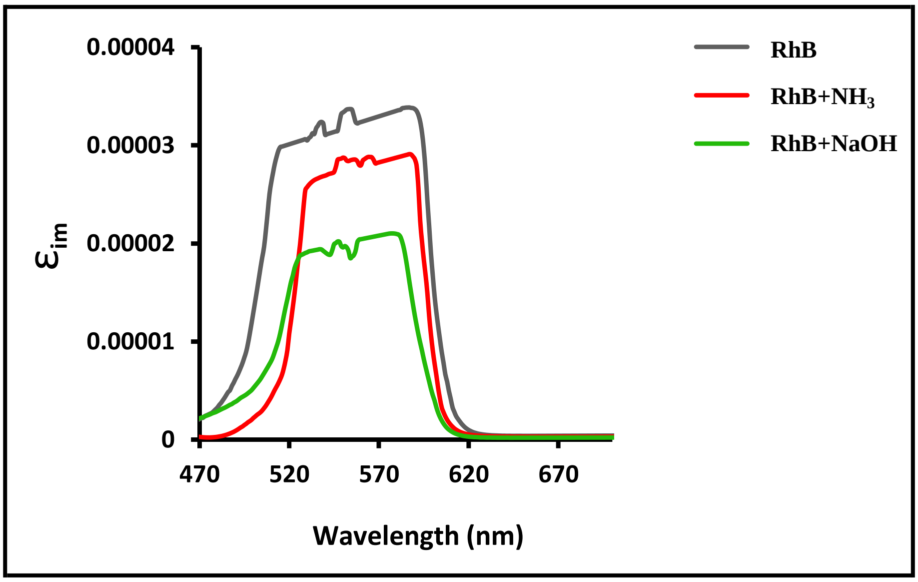


Figure (4.55): Imaginary dielectric constant as a function of wavelength of zwitterionic form for RhB dye solution at concentration (10^{-4}) M.

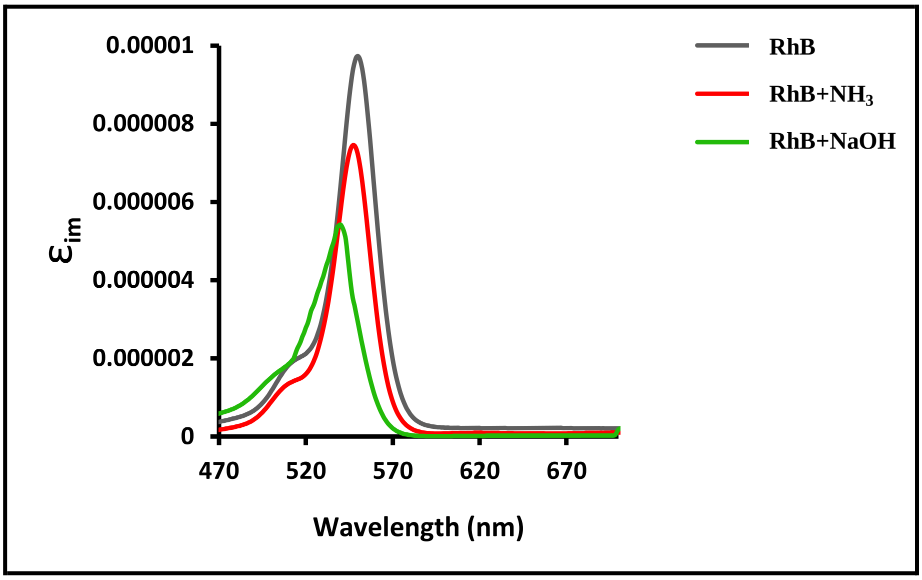
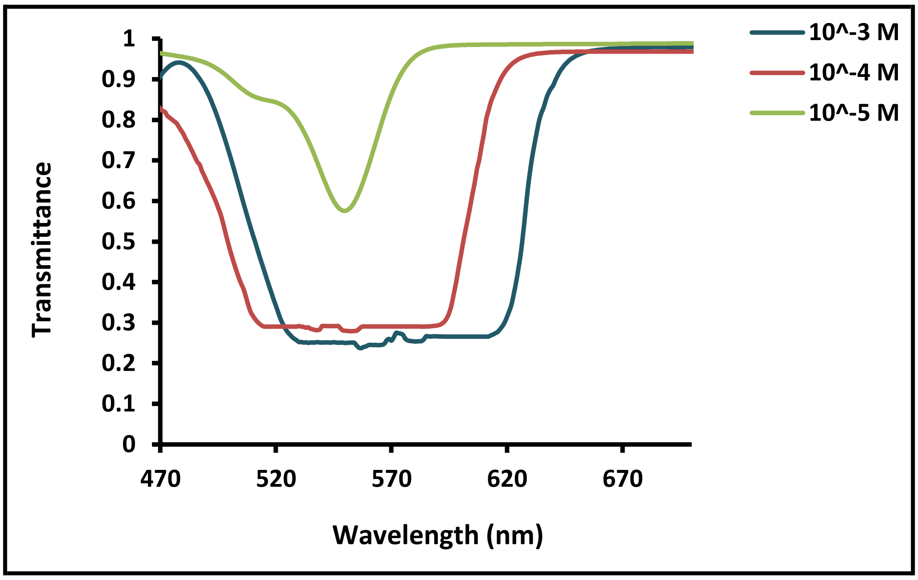


Figure (4.56): Imaginary dielectric constant as a function of wavelength of zwitterionic form for RhB dye solution at concentration (10^{-5}) M.

By observing the absorbance spectra of the cationic and zwitterionic form, it was found that increasing the absorbance leads to an increase in the dielectric constant, because the dielectric constant measures the ability of a solvent to reduce the electric field strength surrounding a charged particle immersed in it, so a solvent with a large dielectric constant will hinder the electrostatic repulsion between the π-xanthine system and the carboxyphenyl group[137,128]. While the decreases of absorptivity in the zwitterionic form lead to decreasing in the dielectric constant that reduce the electrostatic effect of (COO^-) on the chromophore [21] . This shift dependent on the concentration of (H^+) ions in the solution[126].

4.2.8 Transmittance spectra

The transmittance spectra of pure RhB dye solution with different concentrations is shown in figure (4.57).This figure show that the minimum value of transmittance decreases with increase the dye concentration, which is in agreement with Beer-Lambert law.



Figure(4.57): Transmittance spectra as a function of wavelength of pure RhB dye solution at different concentrations.

The transmittance spectra of cationic form of RhB dye solution having different concentration (10^{-3}, 10^{-4} and 10^{-5}) M are shown in figures (4.58-4.60) respectively.

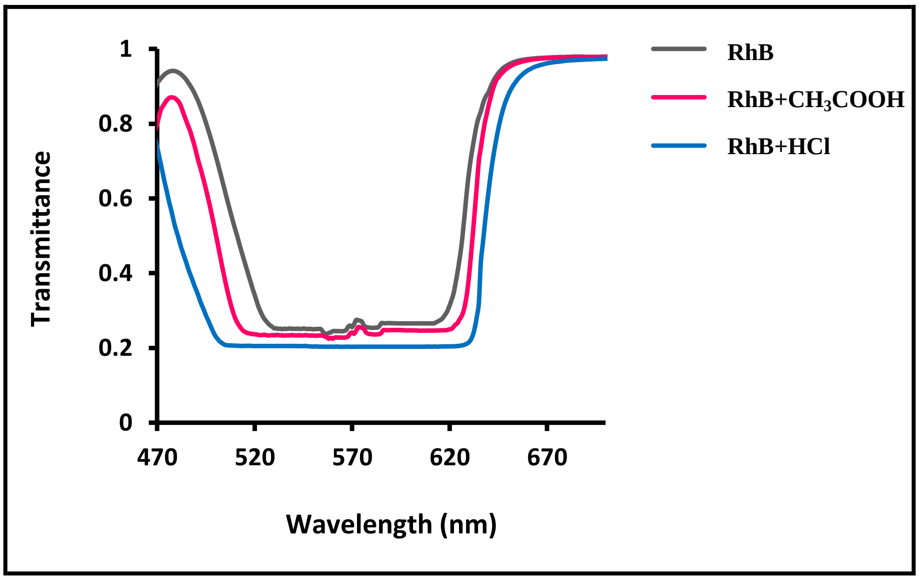


Figure (4.58): Transmittance spectra as a function of wavelength of cationic form for RhB dye solution at concentration (10^{-3} M).

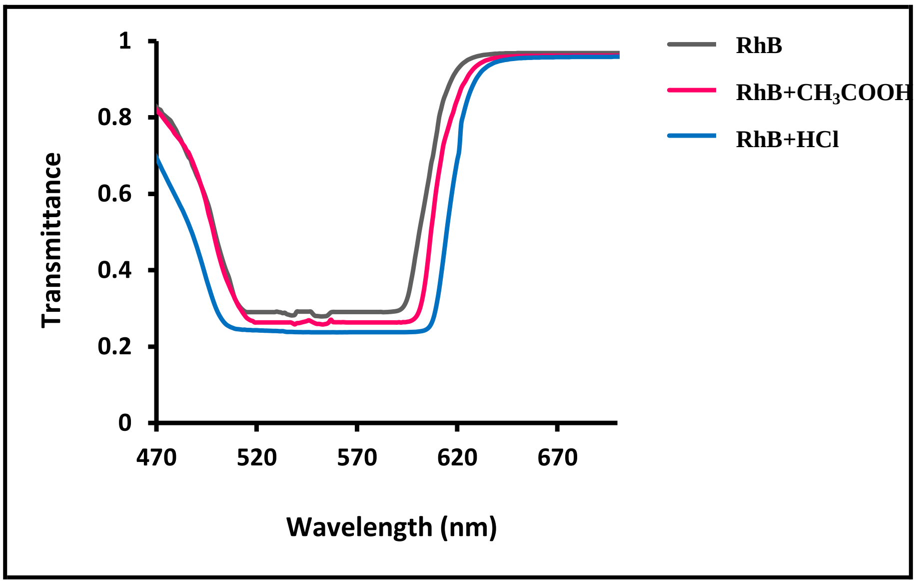


Figure (4.59): Transmittance spectra as a function of wavelength of cationic form for RhB dye solution at concentration (10^{-4} M).

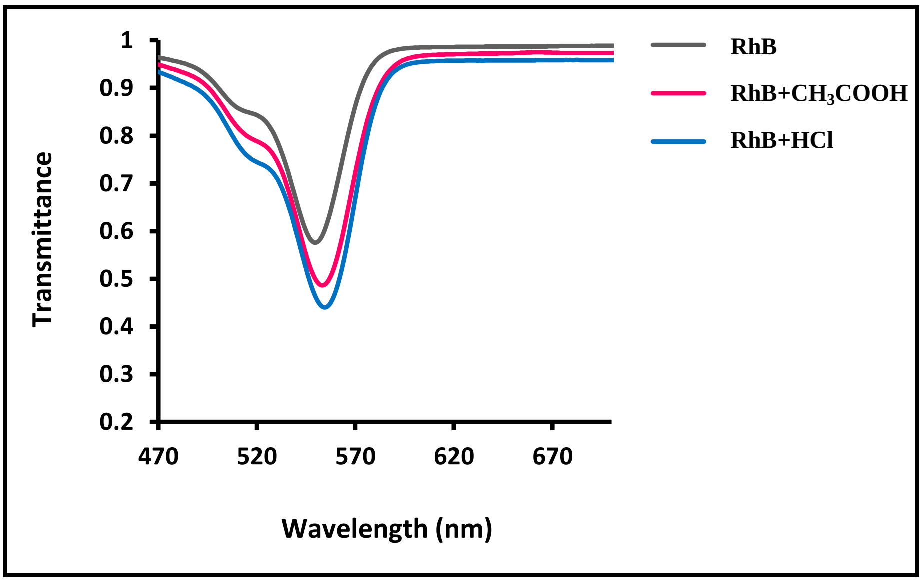


Figure (4.60): Transmittance spectra as a function of wavelength of cationic form for RhB dye solution at concentration (10^{-5} M).

The transmittance intensity of cationic form was lower than the pure dye, this is suggested to take place because of cationic form contain electrons which can be the absorption of electromagnetic energy of the incident light and travel to higher energy levels. This process is not accompanied by emission of radiation because the traveled electron to higher levels have occupied vacant positions of energy bands, thus part of the incident light is absorbed by the substance and does not penetrate through it. The transmittance of pure dye is less than that of the zwitterion form, this is suggested to take place because of pure dye no free electron (i.e. electrons are linked to atoms by covalent bonds),this is because the breaking of electron linkage and moving it to the conduction band need to photon with high energy [14], as shown in figures (4.61-4.63) respectively.

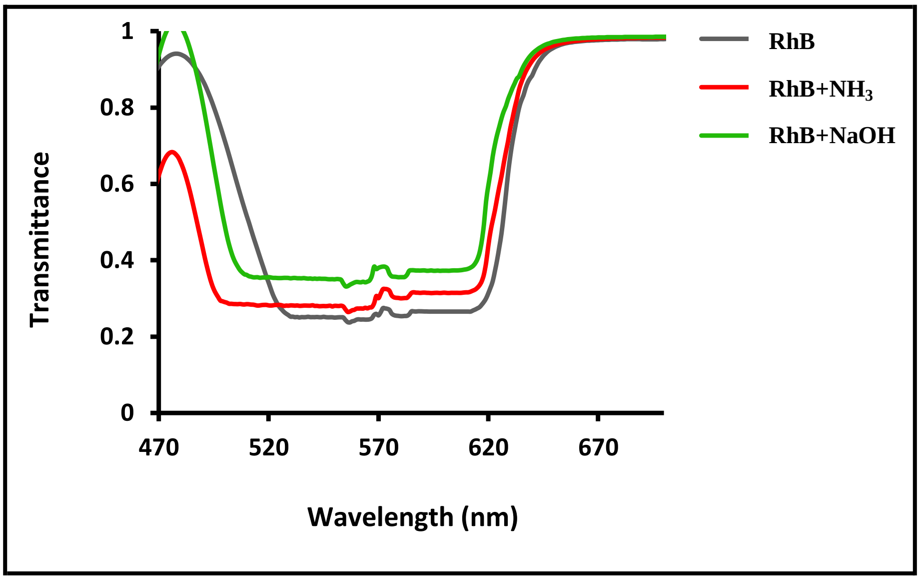


Figure (4.61): Transmittance spectra as a function of wavelength of zwitterionic form for RhB dye solution at concentration (10^{-3}) M.

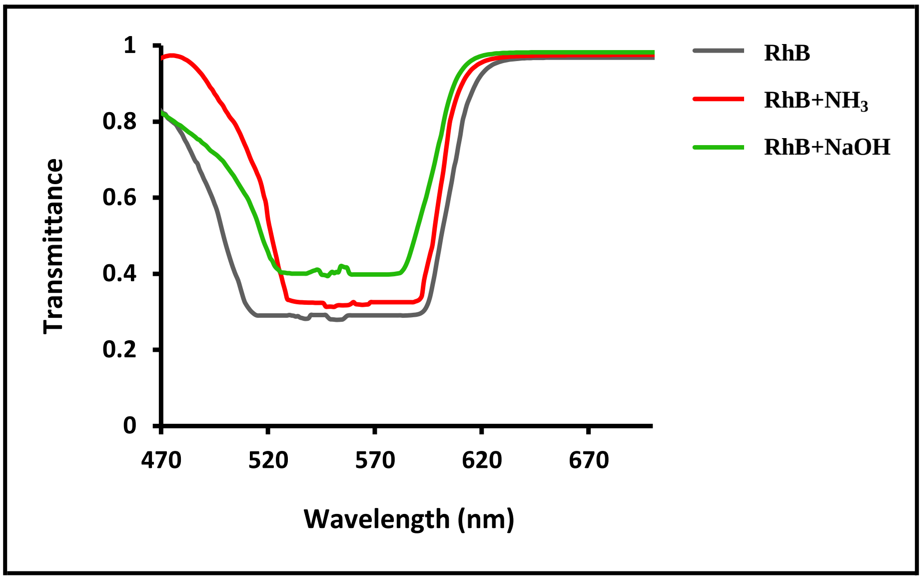


Figure (4.62): Transmittance spectra as a function of wavelength of zwitterionic form for RhB dye solution at concentration (10^{-4}) M.

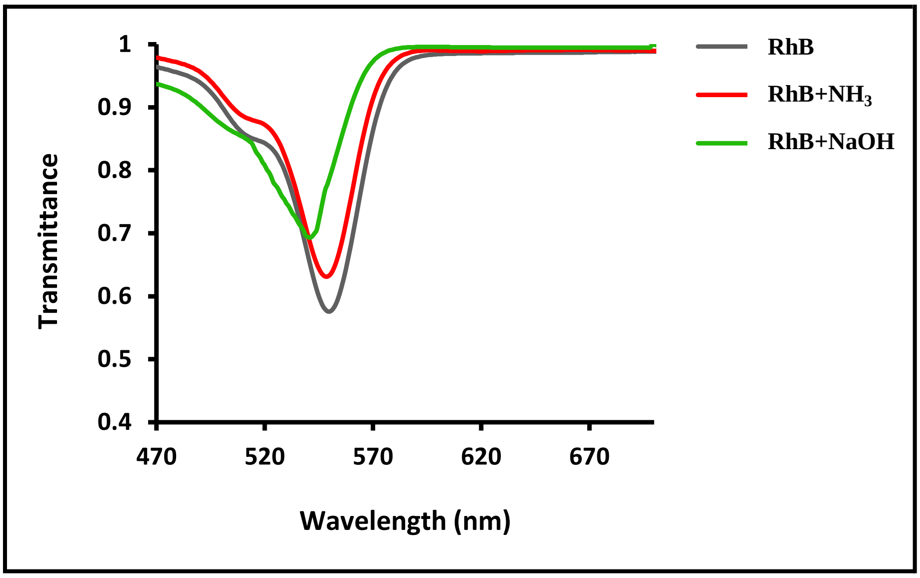


Figure (4.63): Transmittance spectra as a function of wavelength of zwitterionic form for RhB dye solution at concentration (10^{-5}) M.

The linear optical properties of RhB dye solution before and after addition includes, Transmittance, absorption coefficient, refractive index, extinction coefficient, dielectric constant and energy gap that are explained in table (4.2).

Table (4.2): Linear optical parameters of RhB dye solution (before and after) addition at different concentrations.

Solution	C (M)	T	α_o $(cm)^{-1}$	n_o	$K\times10^{-6}$	ε		Eg	
						ε_{real}	$\varepsilon_{im}\times10^{-5}$	Eg allowed	Eg forbidden
RhB	10^{-3}	0.23	1.43	3.24	6.33	10.54	4.14	1.92	1.95
	10^{-4}	0.27	1.27	2.99	5.59	8.99	3.36	2.01	2.02
	10^{-5}	0.57	0.55	1.99	2.44	3.96	0.97	2.14	2.16
RhB + HCL	10^{-3}	0.20	1.59	3.49	7.16	12.24	5.01	1.87	1.92
	10^{-4}	0.23	1.43	3.24	6.41	10.54	4.16	1.98	1.99
	10^{-5}	0.44	0.82	2.34	3.62	5.49	1.70	2.11	2.12
RhB + CH_3COOH	10^{-3}	0.22	1.49	3.33	6.63	11.12	4.42	1.90	1.94
	10^{-4}	0.25	1.35	3.11	5.96	9.72	3.71	2.0	2.01
	10^{-5}	0.48	0.72	2.21	3.17	4.91	1.40	2.12	2.14
RhB + NaOH	10^{-3}	0.33	1.10	2.74	4.87	7.52	2.67	1.94	1.98
	10^{-4}	0.40	0.93	2.48	4.06	6.16	2.01	2.06	2.06
	10^{-5}	0.69	0.36	1.72	1.55	2.97	0.53	2.18	2.19
RhB + NH_3	10^{-3}	0.26	1.32	3.07	5.88	9.44	3.61	1.93	1.96
	10^{-4}	0.31	1.16	2.81	5.09	7.93	2.86	2.04	2.04
	10^{-5}	0.63	0.45	1.85	1.98	3.43	0.73	2.16	2.17

From this table we show that the values of linear parameter for (α_o, n_o) are increased with increasing the concentrations of RhB dye solution (before and after) addition, this is due to decreasing number of molecules per volume unit at low concentrations. This results agreement with [38]. It can see from the value of absorption coefficient ($\alpha \leq 10^4$) cm^{-1} in the table that the transition is indirect of all solutions [127].

The variation of ε_{real} depends on the values of n as a result of small values of extinction in comparison with refractive index ($\varepsilon_{real}= n$), whereas (ε_{im}) mainly depends on the extinction values which are related to the variation of absorption coefficient [136].

The increase in the energy gap in the basic form of the dye relative to the acidic form is small, this value agree with the study in reference [140]. The reduction in optical band gap is associated with the increase in refractive index. The decrease in the optical band gap can be related to an increase in optical dielectric constant. An increase in an optical dielectric constant means the introduction of more charge carriers to the dye and thus an increase in the density of states [136].

4.2.9 Fluorescence spectra

The fluorescence spectra of many organic dyes in liquid solution depend on the local electric field which is induced by the surrounding polar solvent molecules, so this effect is a result of intermolecular solute-solvent interaction forces (such as dipole-dipole or dipole-induced dipole) that tend to stretch the molecular bonds and shift the charge distribution on molecules and thus altering the energy difference between the ground and excited states of the solute molecules. Spectroscopic studies on solutions of polar molecules in polar solvent show that the absorption peak of a solute undergoes red shift in the absorption wavelength as the solvent polarity increases, that mean the dipole-dipole interaction is effective [15].

The fluorescence spectra for RhB dye solution before and after addition at different concentrations (10^{-3}, 10^{-4} and 10^{-5}) M in methanol solvent at room temperature is shown in Figure (4.64).

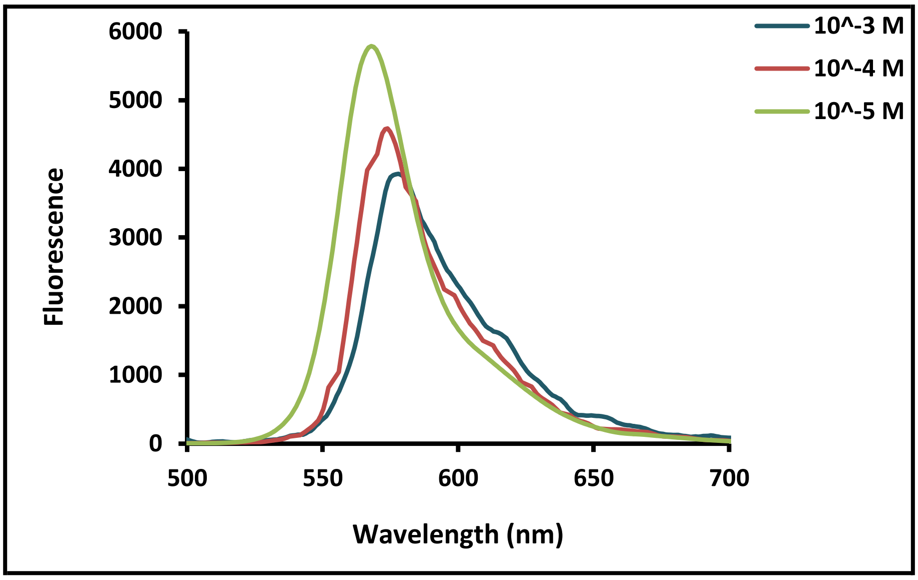


Figure (4.64): Fluorescence spectra as a function of wavelength of pure RhB dye solution different concentrations.

It has been found the fluorescence intensity of dye decreases with increase of the dye concentration. The dependence of the fluorescence intensity on the concentration, may by explained as follows: at higher concentration, the bimolecular competing processes to the molecular fluorescence, such as self- absorption (re-absorption and re-emission of emitted fluorescent photons), and dimmer (and possibly higher aggregates) formation of the dye molecules, play more important rule. This will ultimately reduce the fluorescence emission intensity. It noticed also that there is a red shift of the fluorescence spectra, which increases as the concentration of RhB dye increase. This red shift can be attributed to the self-absorption which modifies the observed fluorescence spectrum by reducing the intensity of the short wavelength region of the spectrum (due to overlap with the absorption spectrum) and enhancing the intensity of the long wavelength region [138].

The emission maximum in the luminescence spectrum will depend on the surrounding medium pH to which Rhodamine B molecules are exposed to [8]. With pH decreases will be increase in the concentration which leads to shift in fluorescence spectra is toward long wave lengths (low energy) attributed to the change of RhB form from its neutral to the cationic [33].

The increase in the (S_1-S_o) energy gap in the basic form of the dye is small, relative to the acidic form, nonradiative rates generally decrease exponentially with increasing energy gap and so this may be sufficient to reduce internal conversion by the observed factor in the basic form of the dye [140]. Thus, it reduces the rate of radioactive emission (fluorescence) [24]. This explains the red shift on the emission spectra shows in the following figures, Which is consistent with suggested in the study [139].

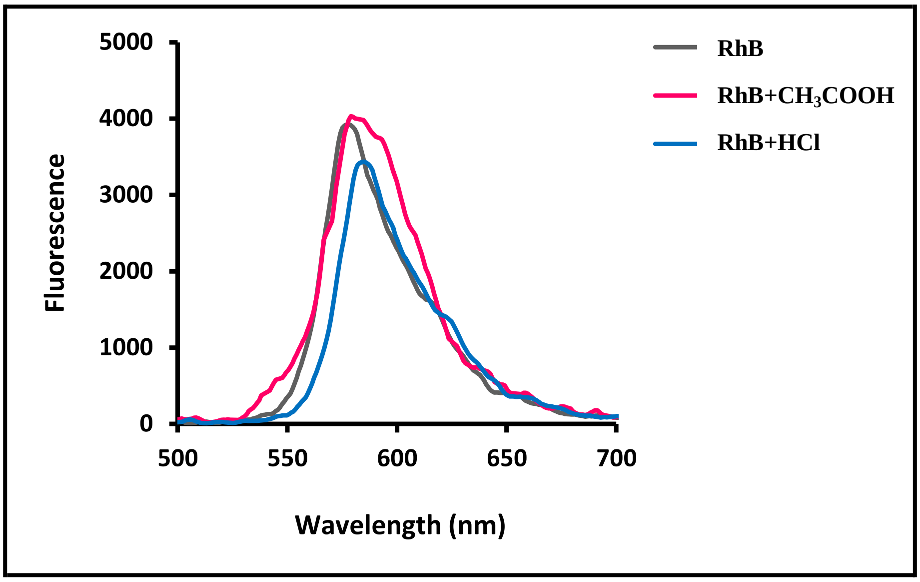


Figure (4.65): Fluorescence spectra as a function of wavelength of cationic form for RhB dye solution at concentration (10^{-3}) M.

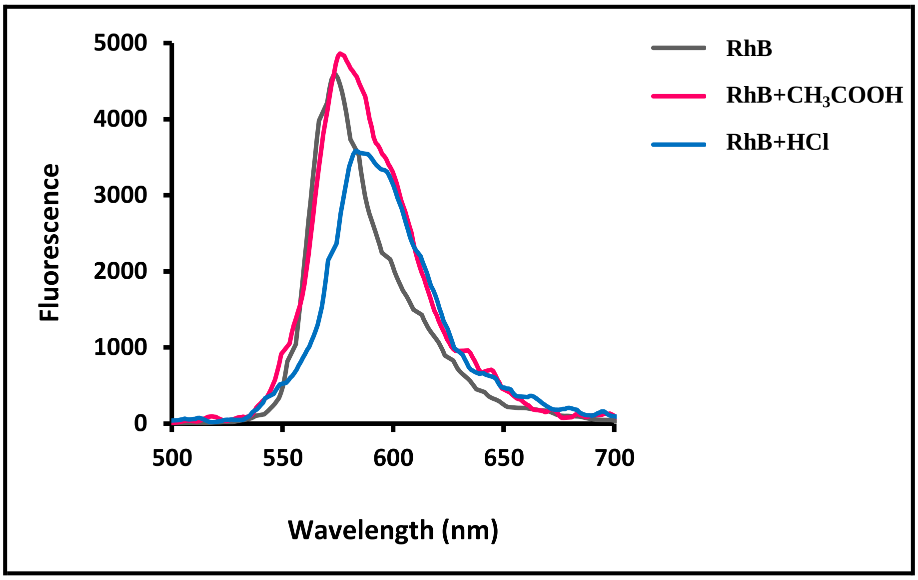


Figure (4.66): Fluorescence spectra as a function of wavelength of cationic form for RhB dye solution at concentration (10^{-4}) M.

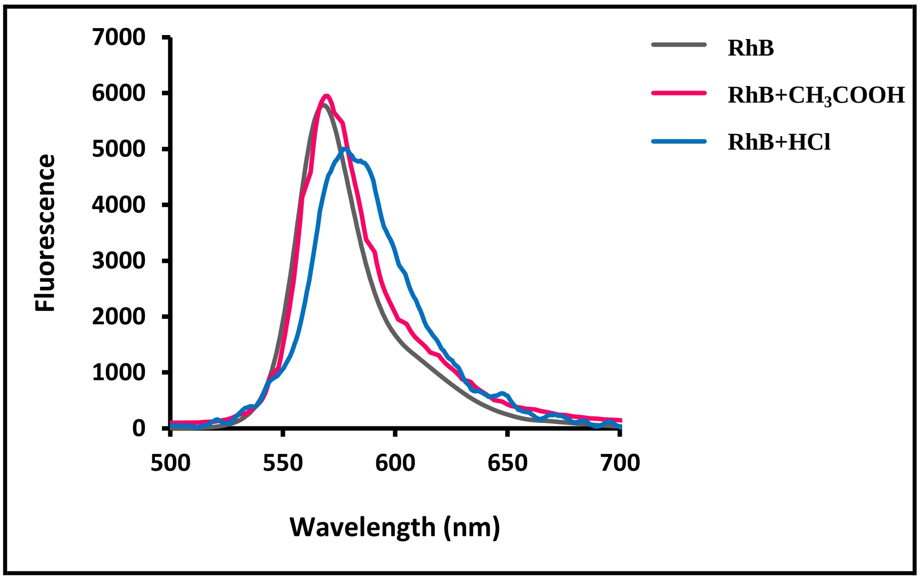


Figure (4.67): Fluorescence spectra as a function of wavelength of cationic form for RhB dye solution at concentration (10^{-5}) M.

Since the ground state of the basic form of the dye has greater solvent stabilization than the ground state of the acid form, so the T_1–S_0 energy gap for basic form would be higher. This explains the blue shift on the emission spectra in the figures (4.68-4.70) [8]. It is also consistent with mentioned in the study [139].

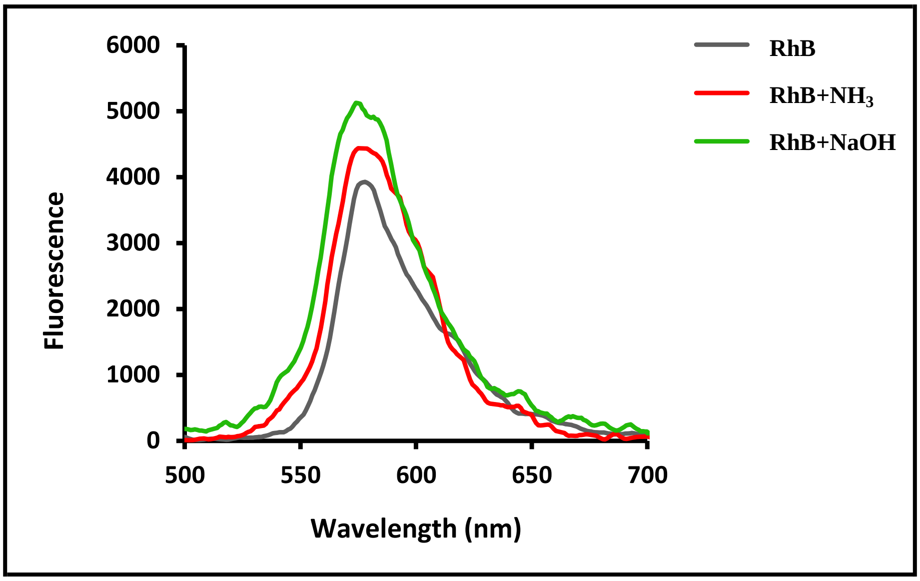


Figure (4.68): Fluorescence spectra as a function of wavelength of zwitterionic form for RhB dye solution at concentration (10^{-3}) M.

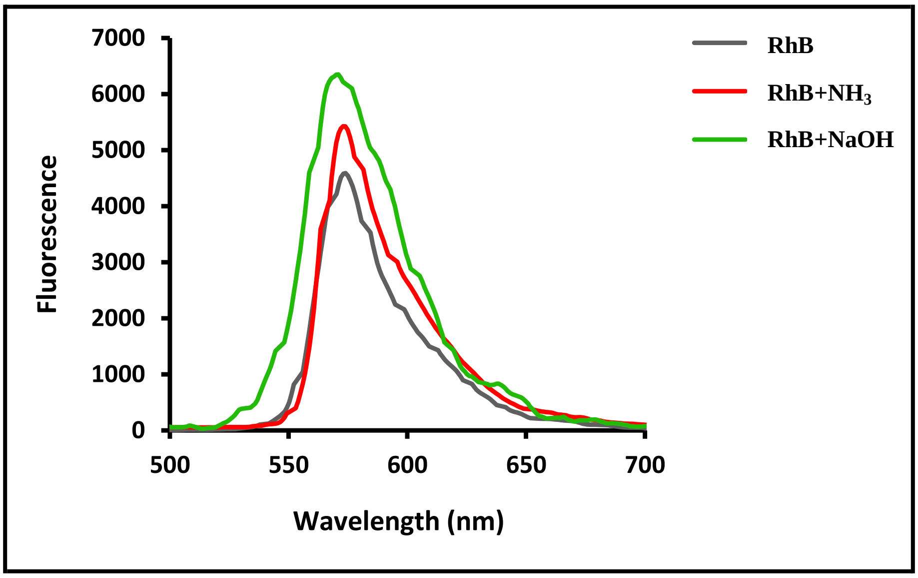


Figure (4.69): Fluorescence spectra as a function of wavelength of zwitterionic form for RhB dye solution at concentration (10^{-4}) M.

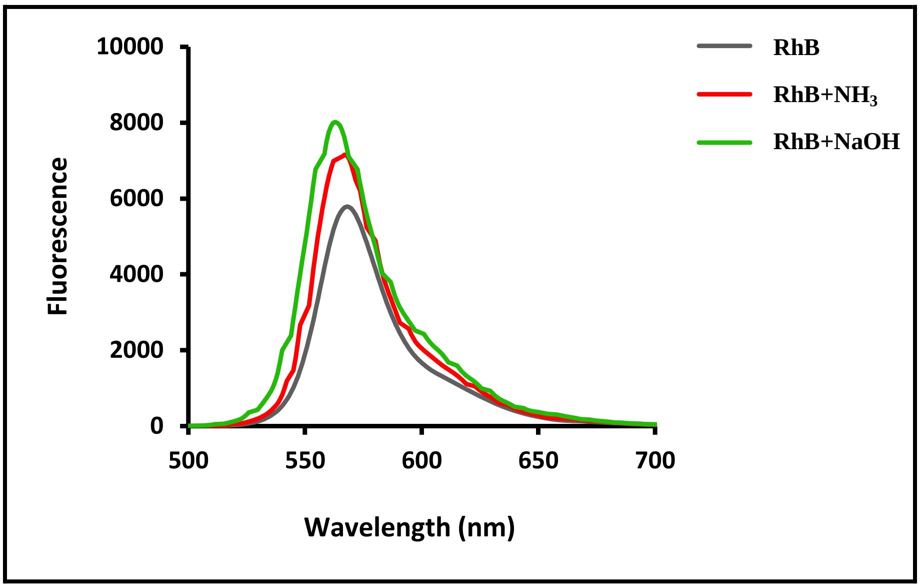


Figure (4.70): Fluorescence spectra as a function of wavelength of zwitterionic form for RhB dye solution at concentration (10^{-5}) M.

It was observed that, in the spectra of cationic form, they have lower intensity and narrower band width than pure dye solution because of RhB dye formed as salts with Cl . This Cl quenches the excited-state dye molecules by acharge-transfer interaction, the quenching can occur via an internal conversion to the charge-transfer singlet excited states, which can be followed by an intersystem crossing with the charge-transfer triplet states. When CH_3COOH were added to the RhB dye solution, increase was not observed in the laser intensity. The addition of NaOH to RhB dye solution resulted in increases in the laser output due to the interrupted aggregation caused by the addition of NaOH [123,141].

4.3 Calculation of Quantum Efficiency and Life Time

The difference in wavelength between the band maxima of absorption and fluorescence spectra is called the Stokes shift. The overlap between absorption and fluorescence spectra of pure RhB dye solution with different concentrations (10^{-3}, 10^{-4} and 10^{-5}) M shows in figure (4.71).

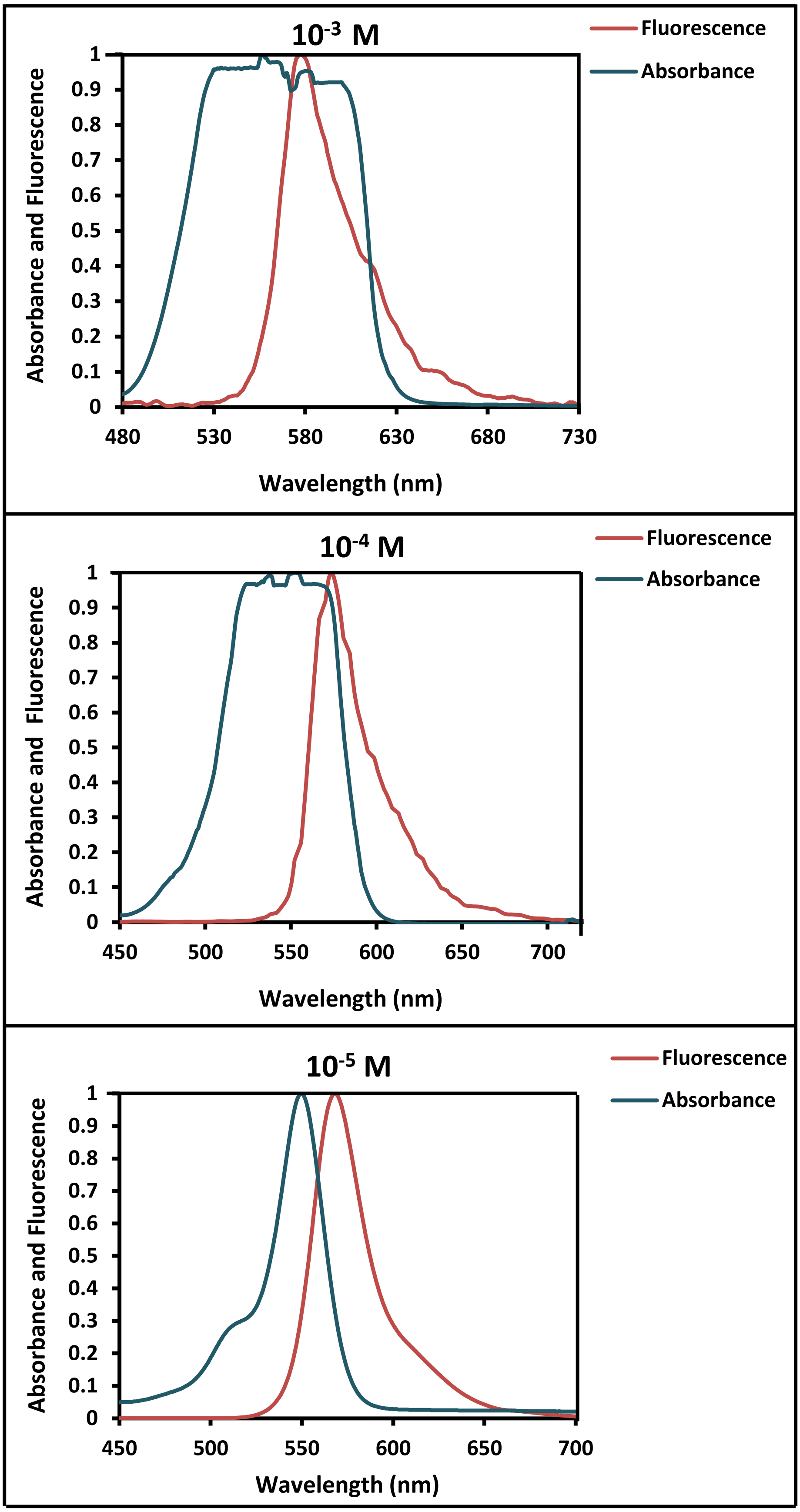


Figure (4.71): The overlap between absorbance and fluorescence spectra of pure RhB dye solution at different concentration.

The Stokes shift is due to the fact that some of the energy of the excited fluorophore is lost through molecular vibrations (vibrational relaxation and internal conversion) that occur during the brief lifetime of the molecules excited state. This energy is dissipated as heat to surrounding solvent molecules as they collide with the excited fluorophore [142].

By observing the overlap between absorption and fluorescence spectra in the above figures, it found that fluorescence spectra have the characteristic of mismatch of fluorescence peak with absorption peak because of the energy of the absorbed photon is always larger than the energy of the emitted photon. As a result, the wavelength of emission is always longer than that of excitation [50].

Increasing the dye solutions concentration causes an increase in the interference between the absorption and fluorescence spectra. The large magnitude of the Stokes shift indicates that the excited state geometry could be different from that of the ground state. Generally speaking, increases in the Stokes shift value indicates an increase in the dipole moment of the excitation state. In such cases, the relaxed excited singlet-state (S_1) will be energetically stabilized compared to the ground state (S_o) and a significant red shift of fluorescence will be observed [35].

While the Stokes shift is small at concentration decrease and thus the overlap of the absorption and emission spectra is large. This effect is further accentuated when dimers are formed, as the red-shifted absorption occurs beneath the emission spectrum [143].

The overlap between absorption and fluorescence spectra of cationic and zwitterionic forms of RhB dye solution with different concentrations (10^{-3}, 10^{-4} and 10^{-5}) M shows in figure (4.72- 83).

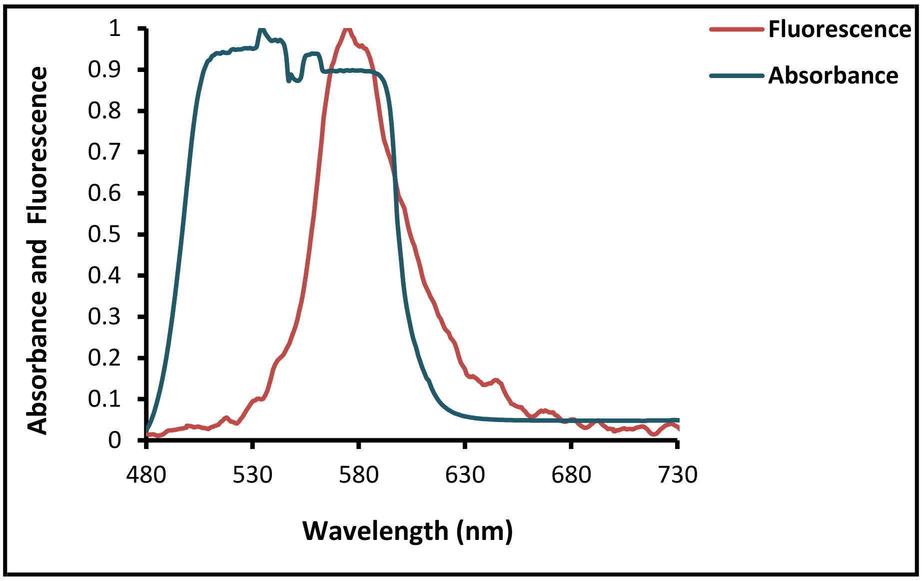


Figure (4.72): The overlap between absorption and fluorescence spectra of (RhB+CH_3COOH) at concentration (10^{-3}) M.

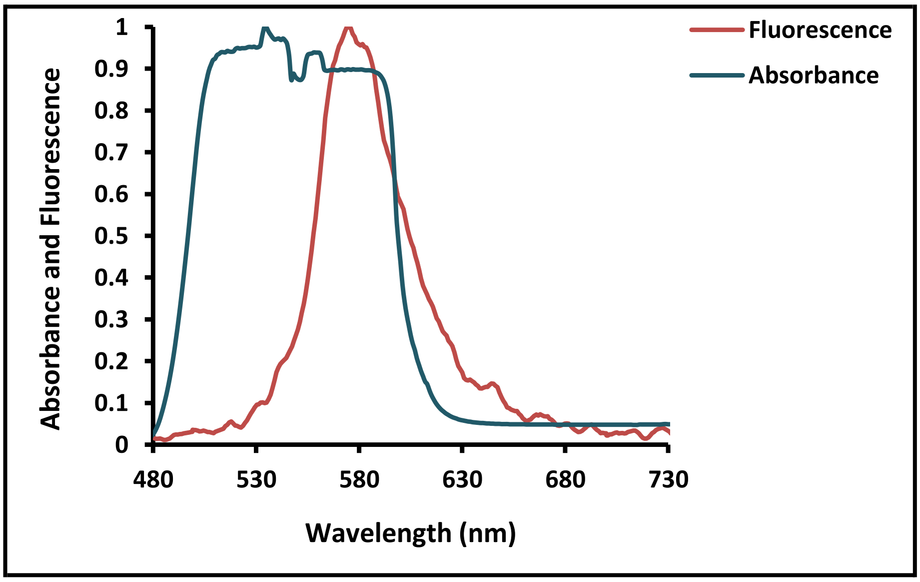


Figure (4.73): The overlap between absorption and fluorescence spectra of (RhB+HCl) at concentration (10^{-3}) M.

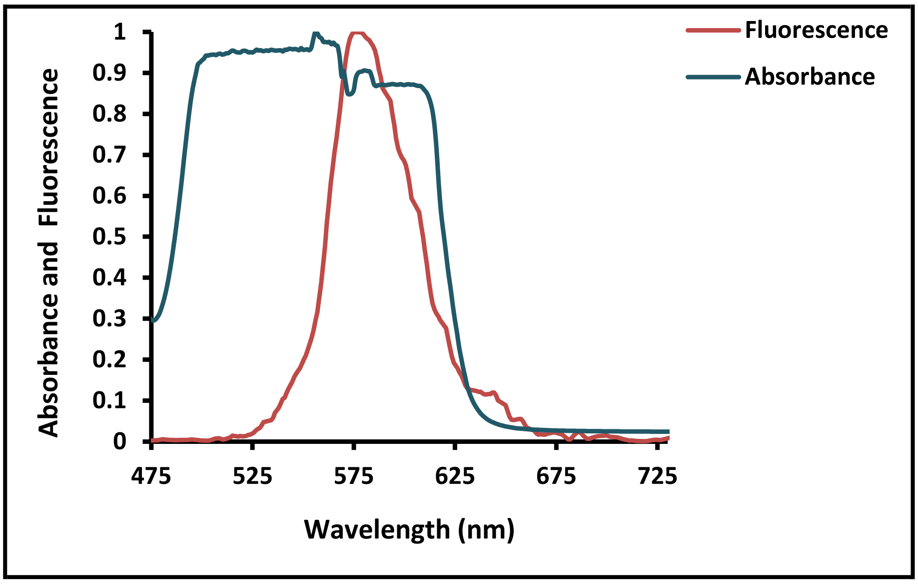


Figure (4.74): The overlap between absorption and fluorescence spectra of (RhB+NH_3) at concentration (10^{-3}) M.

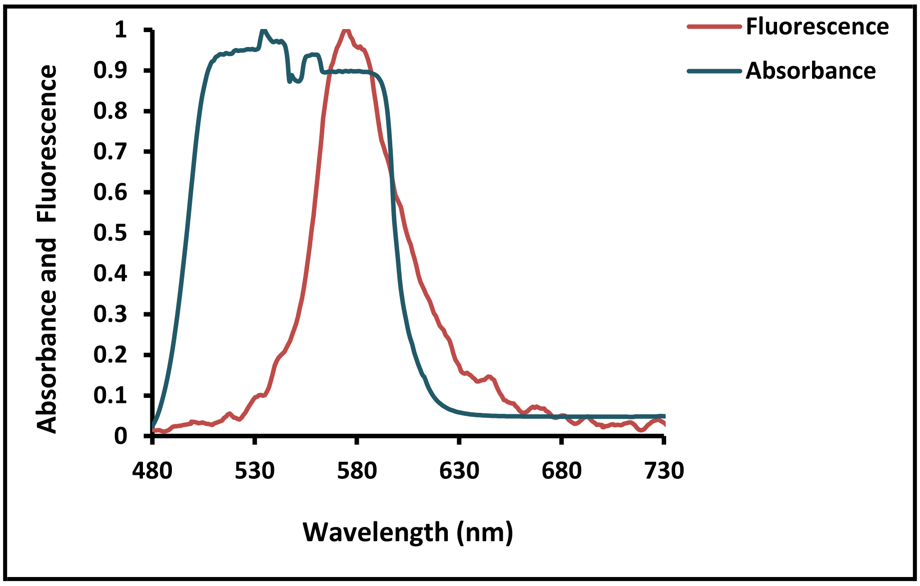


Figure (4.75): The overlap between absorption and fluorescence spectra of (RhB+NaOH) at concentration (10^{-3}) M.

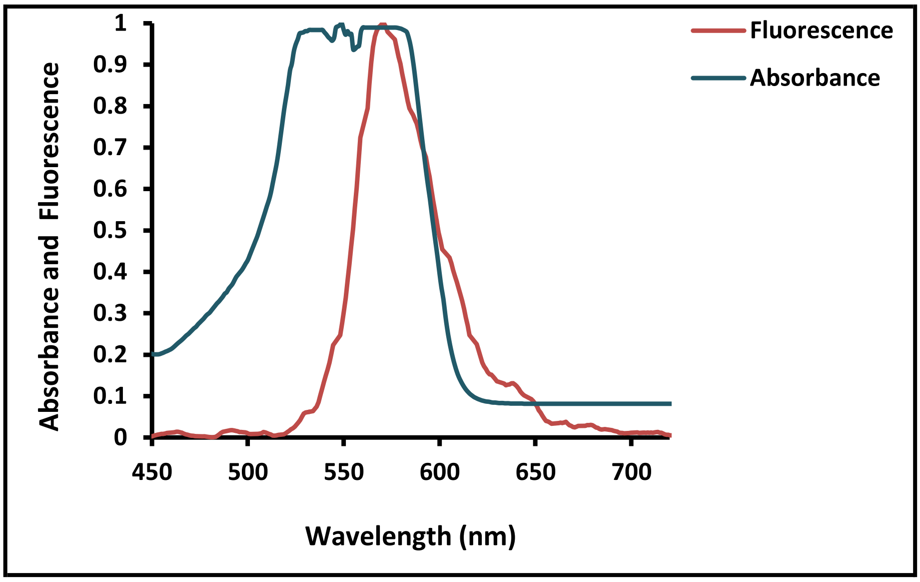


Figure (4.76): The overlap between absorption and fluorescence spectra of (RhB+CH_3COOH) at concentration (10^{-4}) M.

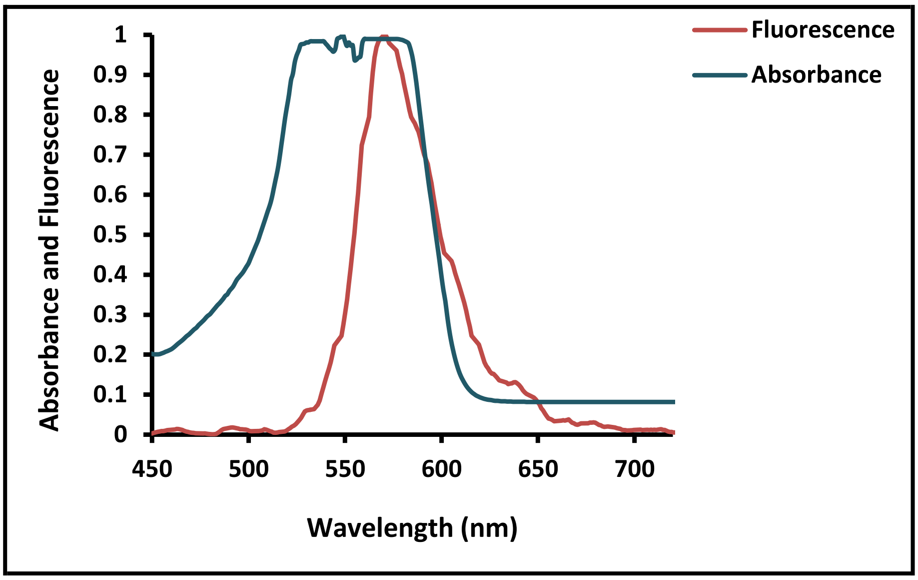


Figure (4.77): The overlap between absorption and fluorescence spectra of (RhB+HCl) at concentration (10^{-4}) M.

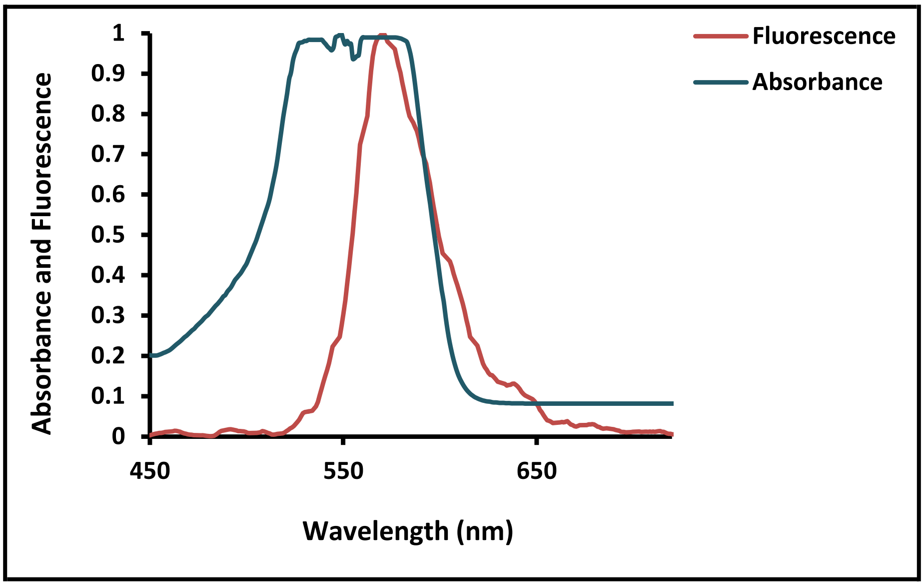


Figure (4.78): The overlap between absorption and fluorescence spectra of (RhB+NH_3) at concentration (10^{-4}) M.

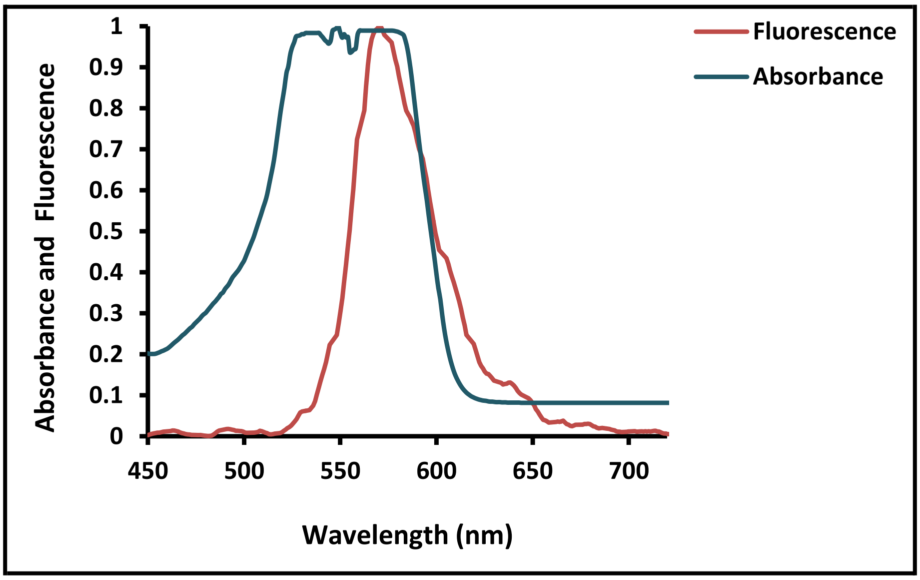


Figure (4.79): The overlap between absorption and fluorescence spectra of (RhB+NaOH) at concentration (10^{-4}) M.

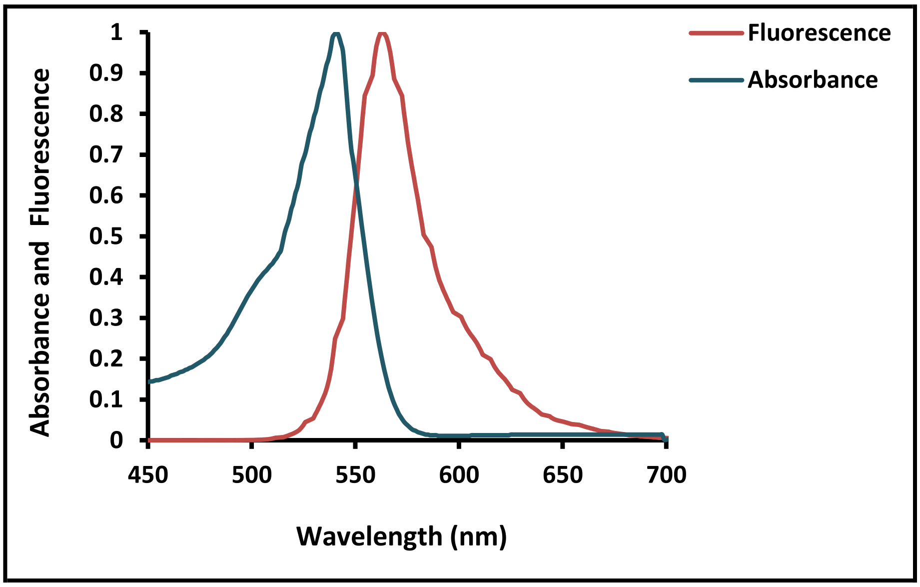


Figure (4.80): The overlap between absorption and fluorescence spectra of (RhB+CH_3COOH) at concentration (10^{-5}) M.

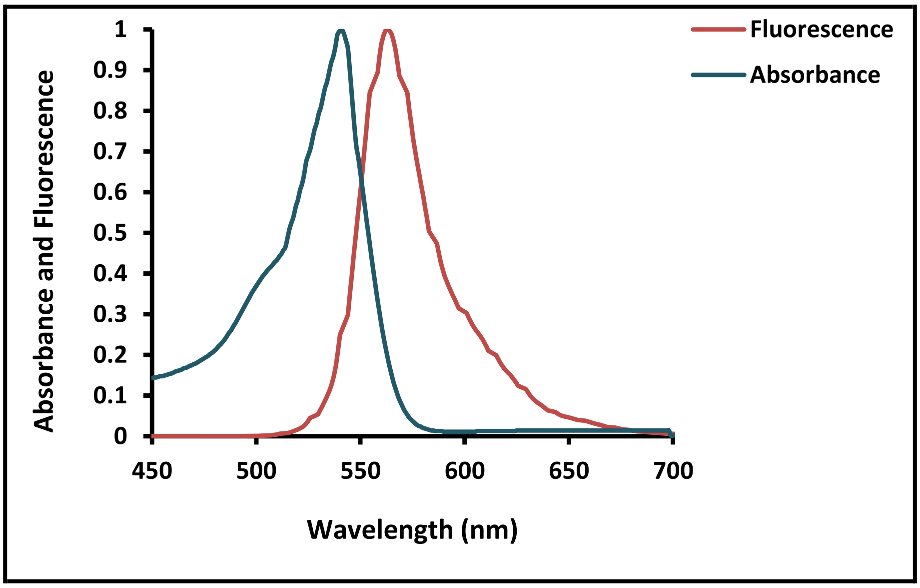


Figure (4.81): The overlap between absorption and fluorescence spectra of (RhB+HCl) at concentration (10^{-5}) M.

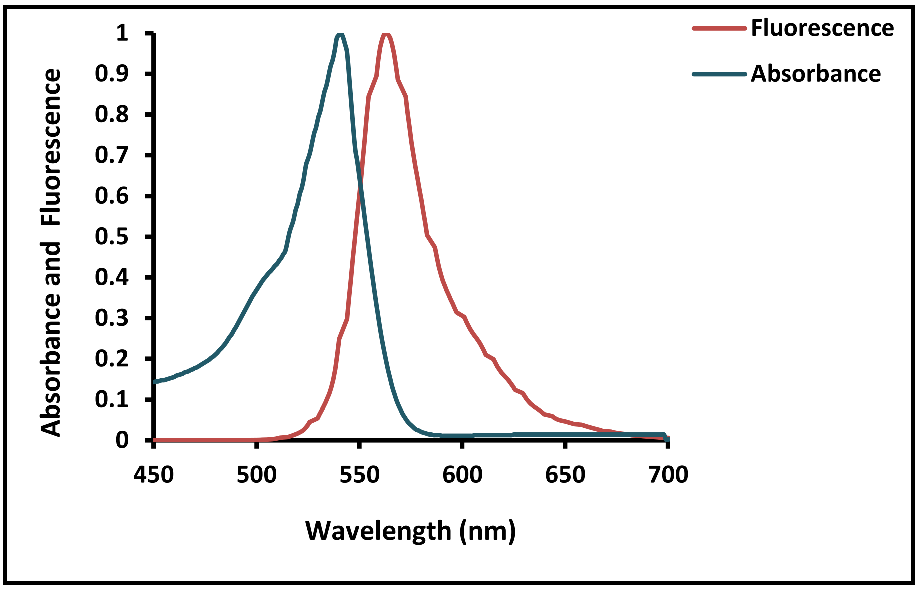


Figure (4.82): The overlap between absorption and fluorescence spectra of (RhB+NH_3) at concentration (10^{-5}) M.

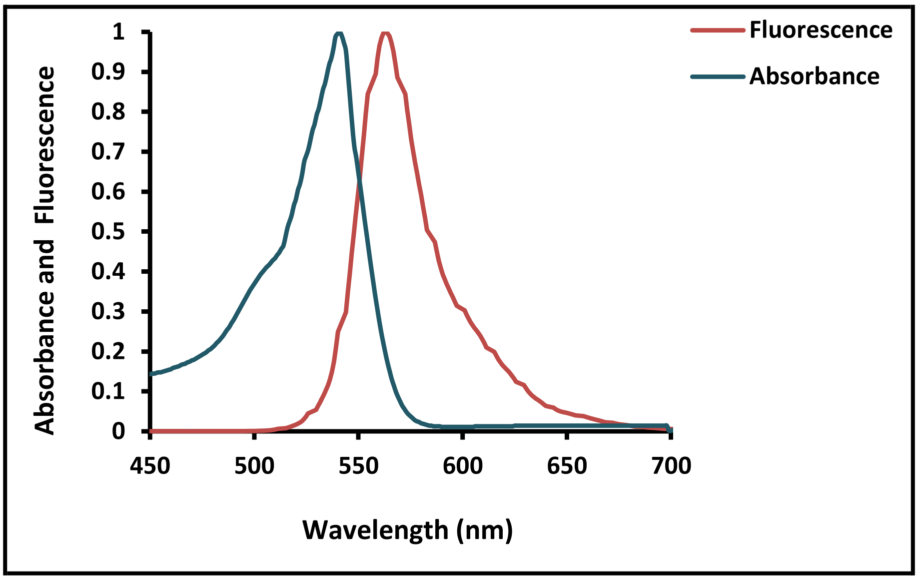


Figure (4.83): The overlap between absorption and fluorescence spectra of (RhB+NaOH) at concentration (10^{-5}) M.

Since their principal chromophores of zwitterionic and cationic are identical, so the spectra of them are very similar, as all the absorption and fluorescence spectra are located very close one to another and thus overlap strongly (i.e the stokes shift is small) [17, 22].

There are many factors that effect on fluorescence of dyes one of which is the concentration, that could affect directly the fluorescence quantum yield and consequently the energy yield of the fluorescence [125]. Life time, non-radiative life time and quantum efficiency have been calculated according to equations (2-8), (2-9) and (2-10) respectively as tabulated in tables (4.3).

Table (4.3): Life Time parameters and quantum efficiency of RhB dye solution (before and after addition) at different concentrations.

Solution	C (M)	T_F (S)	T_{FM} (S)	Q_F
RhB	10^{-3}	0.261	0.483	0.54
	10^{-4}	0.234	0.383	0.61
	10^{-5}	0.216	0.254	0.85
RhB + HCL	10^{-3}	0.262	0.524	0.50
	10^{-4}	0.240	0.413	0.58
	10^{-5}	0.226	0.269	0.84
RhB + CH_3COOH	10^{-3}	0.259	0.470	0.55
	10^{-4}	0.233	0.375	0.62
	10^{-5}	0.211	0.248	0.85
RhB + NaOH	10^{-3}	0.248	0.413	0.60
	10^{-4}	0.215	0.307	0.70
	10^{-5}	0.191	0.209	0.91
RhB + NH_3	10^{-3}	0.252	0.442	0.57
	10^{-4}	0.223	0.327	0.68
	10^{-5}	0.203	0.233	0.87

From the note of the table (4.3), we note the effect of the change of the dye concentration on the life time and the quantum yield of fluorescence, so the effect was that by increasing the concentration, lifetime of the fluorescence increases, and this can be attributed to polarity. The solvent reduces the area of the molecular diffusion of the dye and increases the rate of energy transfers, which leads to an increase in the quantitative output of the fluoridation, this agree with findings in references [28,39]. we note also that the quantum yield of fluorescence for zwitterionic form is larger than the cationic form, which is agreement with the study in references [21,140].

4.4 Nonlinear Optical Properties

The nonlinear optical properties of RhB dye solution before and after addition in methanol solvent for different concentrations (10^{-3}, 10^{-4} and 10^{-5}) M were measured by using continuous wave (CW) diode pump solid state blue laser at wavelength (457 nm) and (112mW) power. There are two parts were used to measure the nonlinear properties of the material by Z-Scan technique. The first part is open-aperture Z-Scan and the second part is the closed-aperture Z-Scan.

4.4.1. Nonlinear absorption coefficient

The nonlinear absorption coefficient of RhB dye solution before and after addition were measured by open-aperture Z-Scan technique. The performed open aperture Z-Scan exhibits an increasing in the transmittance about the focus of the lens. The normalized transmittances of Open-aperture Z-Scan measurements as a function of distance of pure RhB dye solution at different concentrations is shown in figure (4.84). The transmittance show two photon absorption phenomenon (its noticed RSA characteristics) because of the excited state has strong absorption compared with that of the ground state. This behavior is reported in the literature [144].

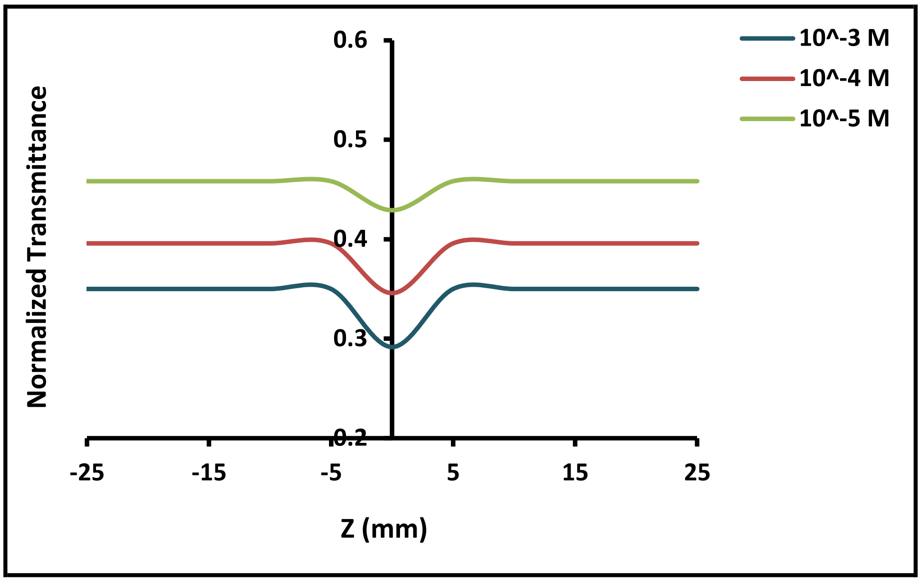


Figure (4.84): Open-aperture Z-Scan data of pure RhB at different concentrations.

The normalized transmittances of Open-aperture Z-Scan measurements as a function of distance of cationic forms of RhB dye solution are shown in figures (4.85-4.87). Its noticed (two photon absorption) phenomenon.

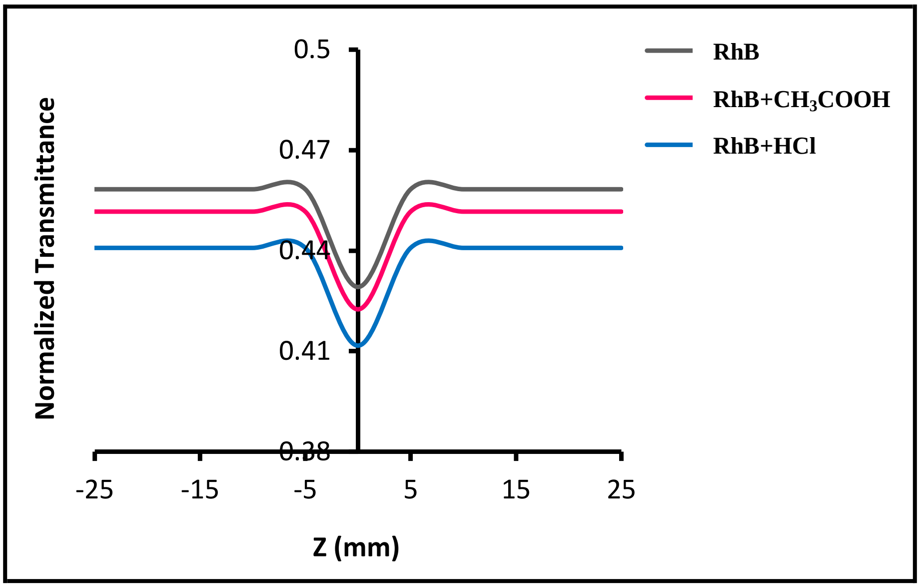


Figure (4.85): Open-aperture Z-Scan data of cationic form for RhB dye solution at concentration (10^{-3}) M.

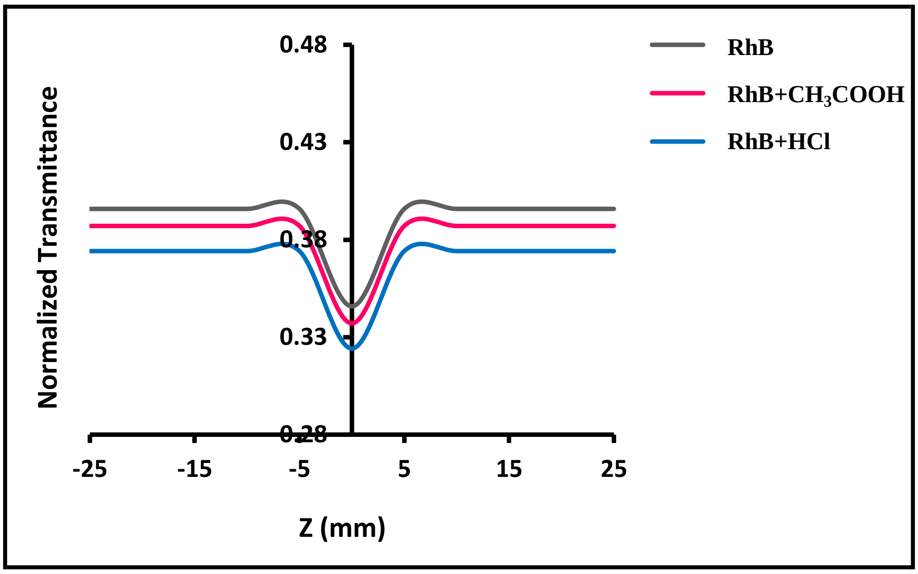


Figure (4.86): Open-aperture Z-Scan data of cationic form for RhB dye solution at concentration (10^{-4}) M.

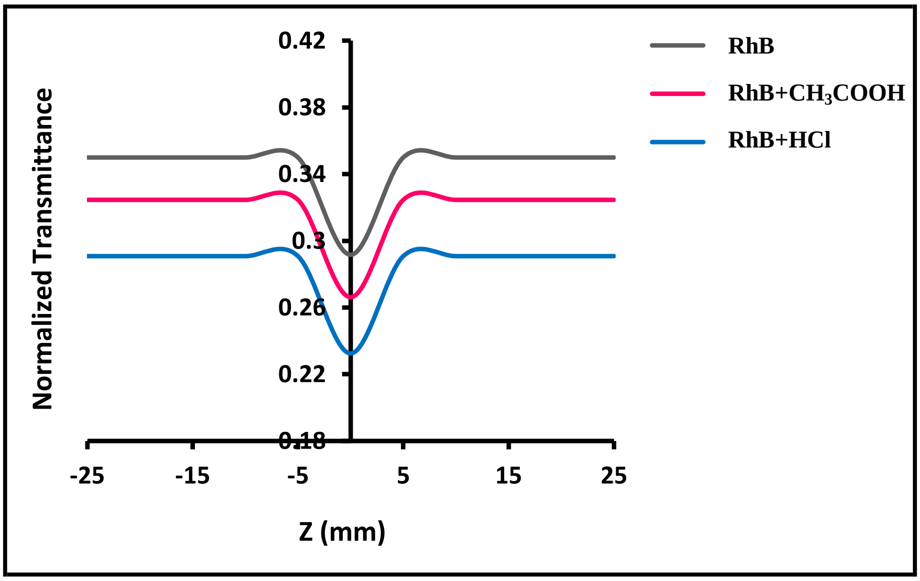


Figure (4.87): Open-aperture Z-Scan data of cationic form for RhB dye solution at concentration (10^{-5}) M.

The normalized transmittances of Open-aperture Z-Scan measurements as a function of distance of zwitterionic forms of RhB dye solution are shown in figures (4.88-4.90). Its noticed (two photon absorption) phenomenon.

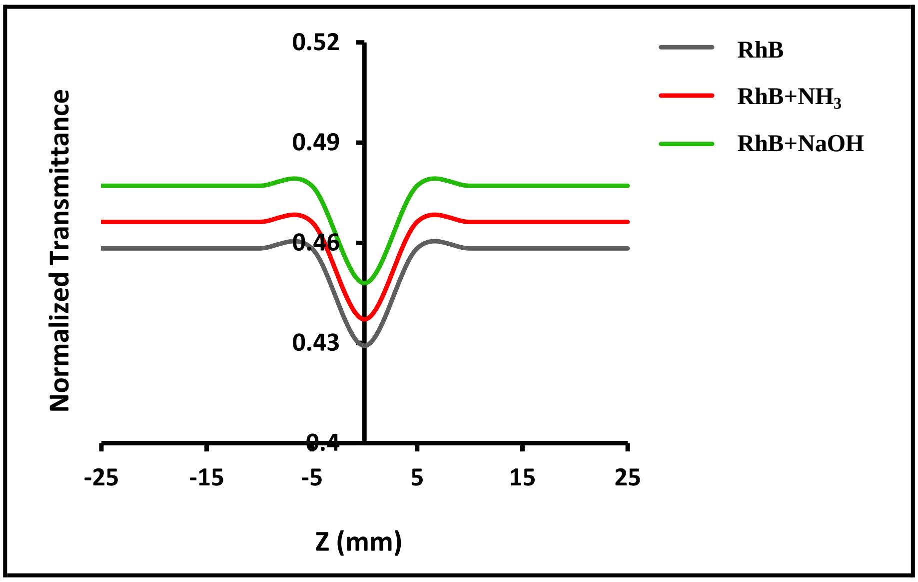


Figure (4.88): Open-aperture Z-Scan data of zwitterionic form for RhB dye solution at concentration (10^{-3}) M.

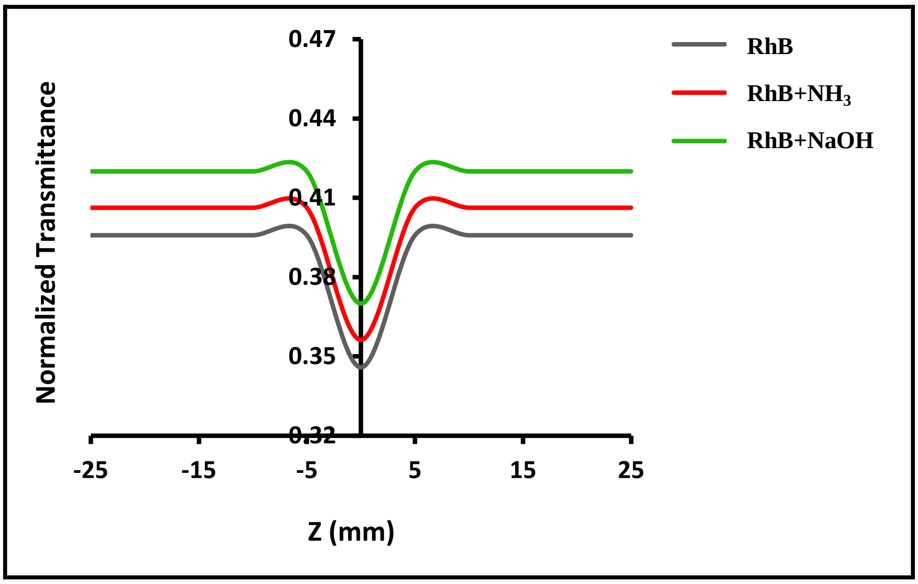


Figure (4.89): Open-aperture Z-Scan data of zwitterionic form for RhB dye solution at concentration (10^{-4}) M.

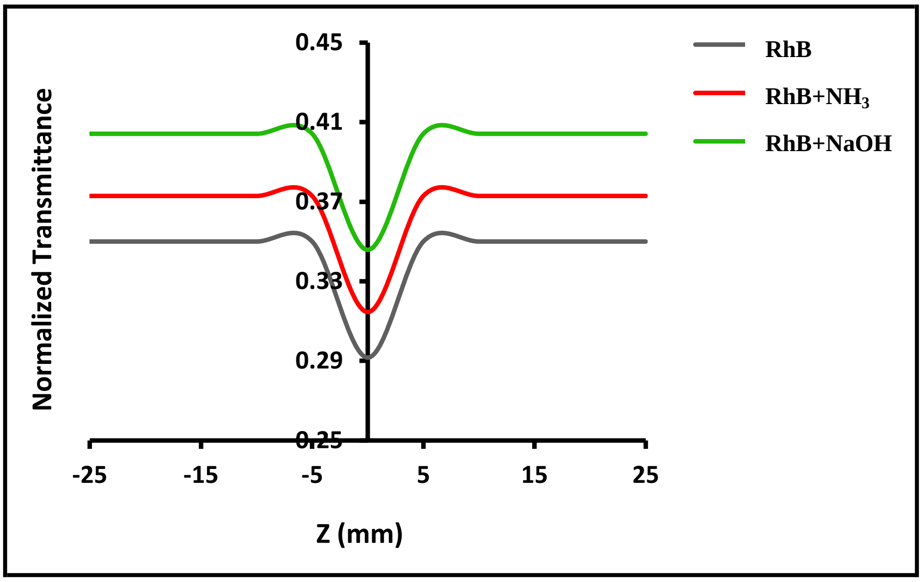


Figure (4.90): Open-aperture Z-Scan data of zwitterionic form for RhB dye solution at concentration (10^{-5}) M.

The behavior of transmittance for all solutions starts linearly at different distances from the far field of the sample position (-Z). At the near field, the transmittance curve begins to decrease until it reaches the minimum value (T_{min}) at the focal point, where (Z=0 mm). The transmittance begins to increase towards the linear behavior at the far field of the sample position (+Z). The change of intensity, in this case, is caused by two photon absorption when in the sample travels through beam waist. The open-aperture Z-Scan defines variable transmittance values, which was used to determine absorption coefficient [145].

4.4.2. Nonlinear refractive index

The nonlinear refractive index of RhB dye solution (before and after addition) in methanol solvent for different concentrations were measured by closed-aperture Z-Scan technique. The normalized transmittances of Close-aperture Z-Scan measurements as a function of distance of pure RhB dye solution at different concentrations is shown in figure (4.91).

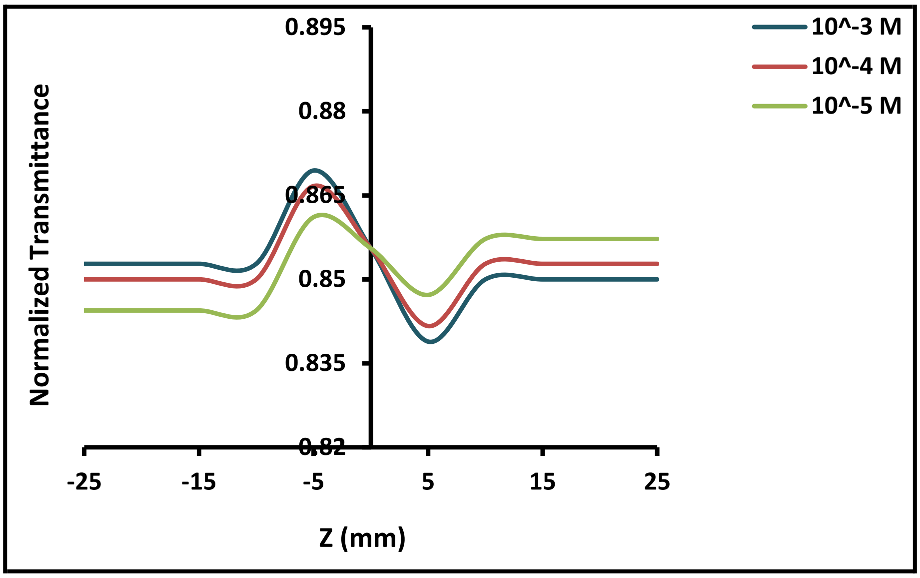


Figure (4.91): Closed-aperture Z-Scan data of pure RhB at different concentrations.

The nonlinear effect region is extended from (-15) mm to (15) mm. The peak followed by a valley transmittance curve obtained from the closed aperture Z-Scan data indicates that the sign of the refraction nonlinearity is negative ($n_2 < 0$), leading to self-defocusing lensing in these samples [144].

The normalized transmittances of Close-aperture Z-Scan measurements as a function of distance of cationic form of RhB dye solution with different concentrations is shown in figures (4.92-4.94).

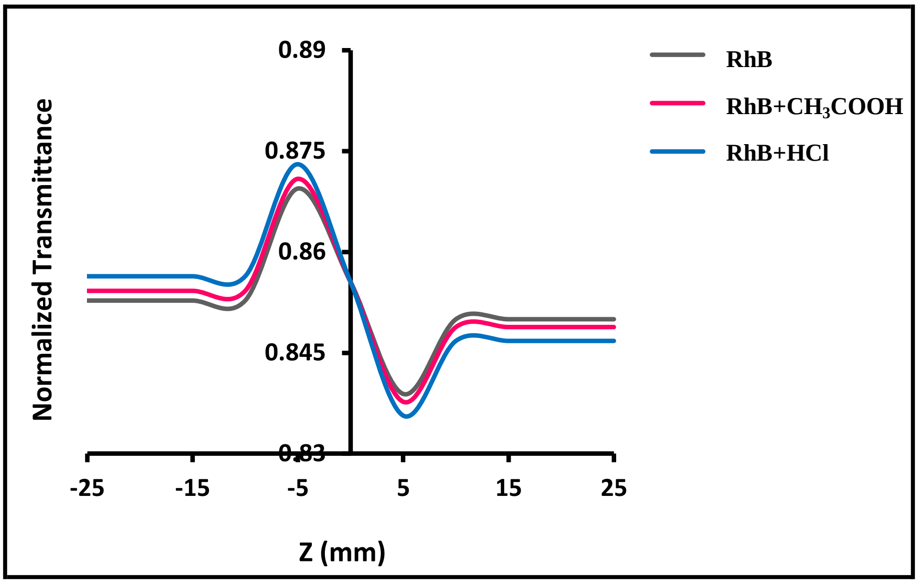


Figure (4.92): Closed-aperture Z-Scan data of cationic form for RhB dye solution at concentration (10^{-3}) M.

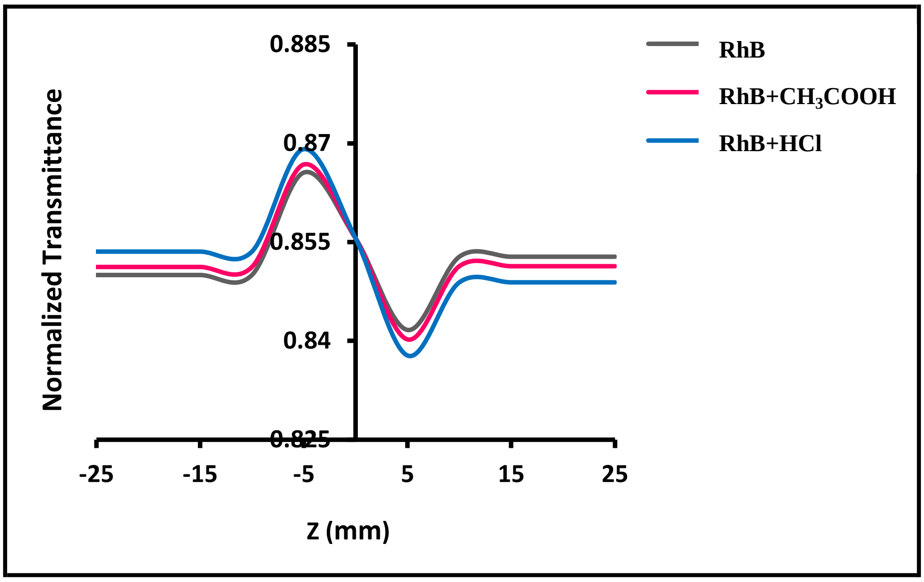


Figure (4.93): Closed-aperture Z-Scan data of cationic form for RhB dye solution at concentration (10^{-4}) M.

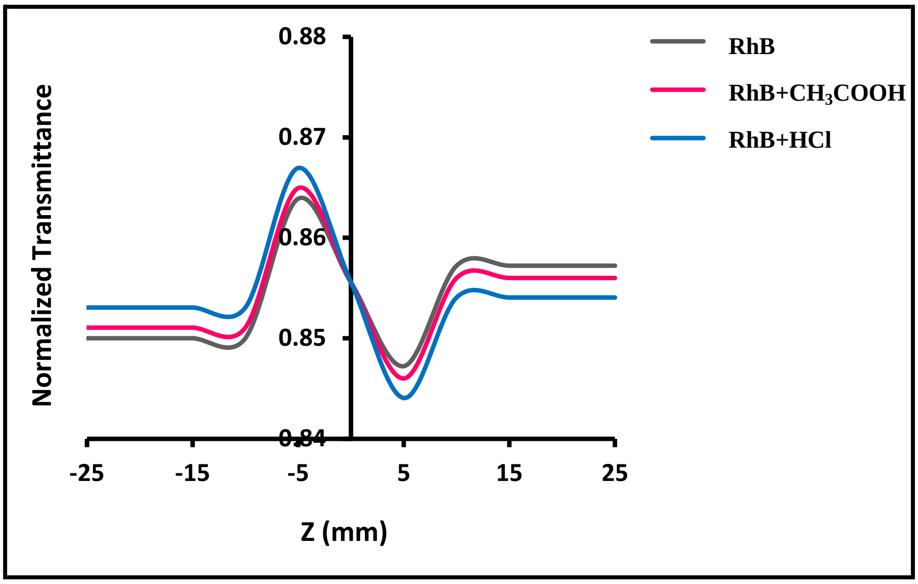


Figure (4.94): Closed-aperture Z-Scan data of cationic form for RhB dye solution at concentration (10^{-5}) M.

The normalized transmittances of Close-aperture Z-Scan measurements as a function of distance of zwitterionic form of RhB dye solution with different concentrations is shown in figures (4.95-4.97).

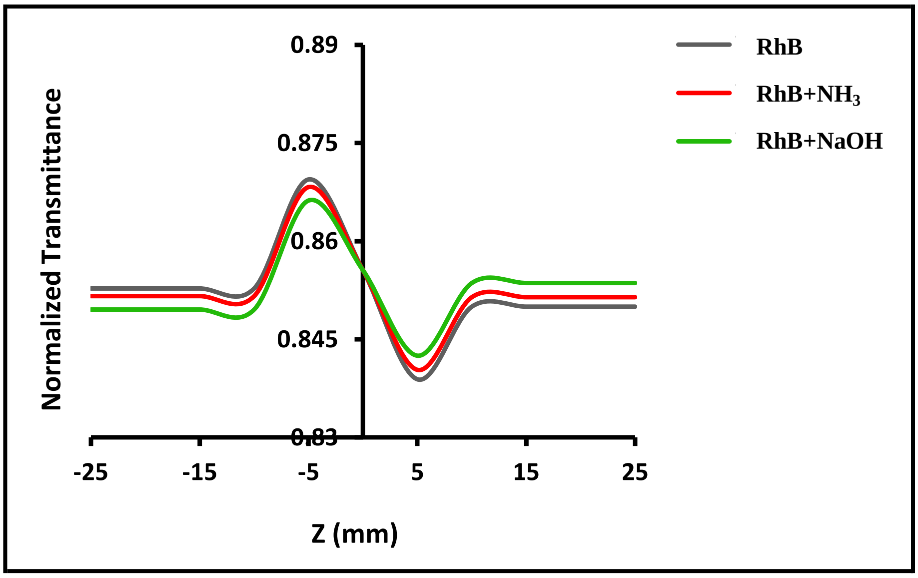


Figure (4.95): Closed-aperture Z-Scan data of zwitterionic form for RhB dye solution at concentration (10^{-3}) M.

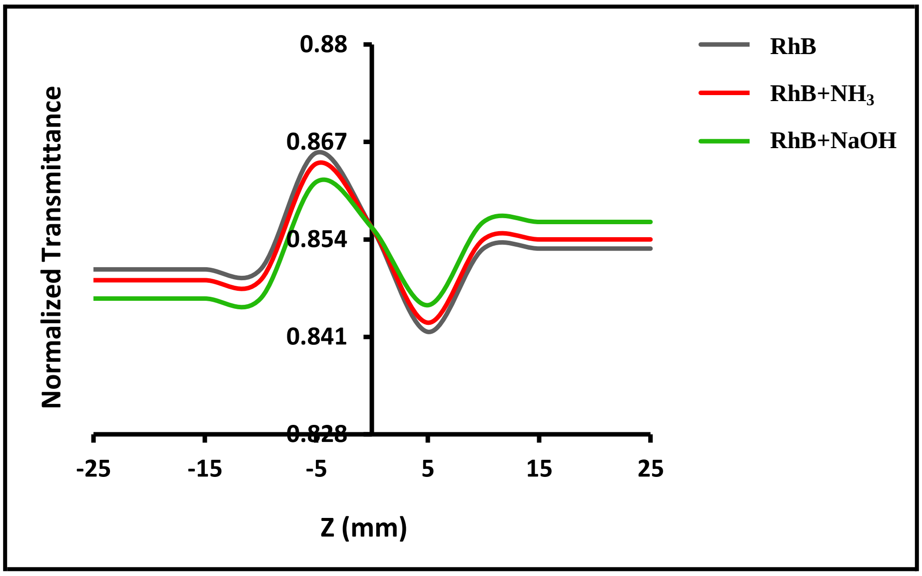


Figure (4.96): Closed-aperture Z-Scan data of zwitterionic form for RhB dye solution at concentration (10^{-4}) M.

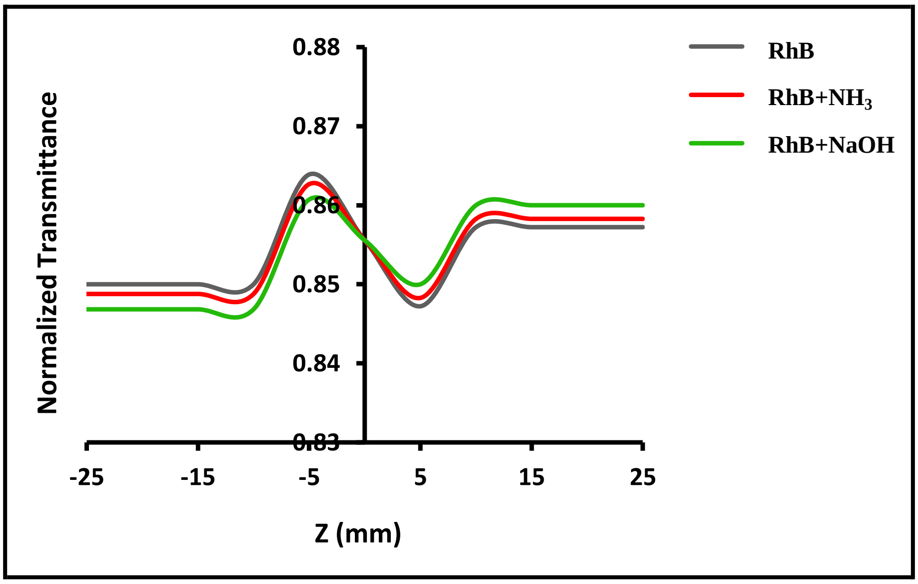


Figure (4.97): Closed-aperture Z-Scan data of zwitterionic form for RhB dye solution at concentration (10^{-5}) M.

The nonlinear refractive index effect may arise from different physical mechanisms such as electronic (Kerr effect) or thermal effect (focusing and defocusing). The nonlinear refractive index for all samples in this case may be attributed to a thermal nonlinearity [146] . The localized absorption of a tightly focused laser pulse propagating through an absorbing dye medium which results in deposition of heat via non-radiative decay from excited states produces a spatial distribution of temperature, density gradients in the dye sample, therefore; it has a larger nonlinear phase shift consequently larger value of the peak to valley transmittance. Consequently, a spatial variation of nonlinear refractive index which acts as a thermal lens will result in a severe phase distortion of the propagating beam [10].

The nonlinear refractive index (n_2) increased with increasing concentration. This may be attributed to the fact that the number of the dye molecules increases when the concentration increases and more particles get thermally agitated resulting in an enhanced effect [10].

The nonlinear parameters of RhB dye solution before and after addition includes nonlinear refractive index and nonlinear absorption coefficient ,are calculated from equations (2-25) and (2-29) respectively ,as tabulated in table (4.4).

Table (4.4): Nonlinear optical parameters of RhB dye solution (before and after) addition at different concentrations.

Solutions	C (M)	T (Z)	$\beta \times 10^{-3}$ cm/mW	$\Delta T_{P\text{-}V}$	$n_2 \times 10^{-11}$ cm^2/mW
RhB	10^{-3}	0.429	0.152	0.030	6.86
	10^{-4}	0.345	0.122	0.023	5.32
	10^{-5}	0.291	0.099	0.016	3.58
RhB + HCL	10^{-3}	0.411	0.147	0.037	8.46
	10^{-4}	0.324	0.115	0.031	7.04
	10^{-5}	0.232	0.080	0.022	4.99
RhB + CH_3COOH	10^{-3}	0.422	0.15	0.033	7.47
	10^{-4}	0.337	0.119	0.026	5.94
	10^{-5}	0.266	0.091	0.018	4.11
RhB + NaOH	10^{-3}	0.447	0.156	0.023	5.24
	10^{-4}	0.37	0.128	0.016	3.60
	10^{-5}	0.345	0.116	0.010	2.28
RhB + NH_3	10^{-3}	0.437	0.154	0.027	6.24
	10^{-4}	0.356	0.125	0.021	4.70
	10^{-5}	0.314	0.106	0.014	3.08

The results show an increase in all the values of (β and n_2) with a increase the concentration, this result can be due to increases in the number of the dye particles with increase the concentration, and the electronic polarization is more resulting which enhanced the nonlinear effect. The results of nonlinear optical properties of pure dye solution agree with the works of the researcher [147]. Also the increase in concentration the excited state absorption cross section increases, thereby leading to an increase in nonlinear absorption [144].

The nonlinear absorption of pure RhB dye is larger than the cationic form because of the excited-state absorption cross-section of pure RhB dye is larger than the cationic form [144,32].

The value of refractive index of cationic form is larger than pure the RhB dye and zwitterion form respectively due to the movement electron π cloud from the acid to the dye group making the molecule highly polarized and thus enhanced the nonlinear effect of the cationic form [148].

4.5 Conclusions

In this work, RhB dye solution (before and after addition) were characterized and studied for possible device applications. The main conclusions that we have obtained in our research:

1.The spectra of zwitterion and cationic are very similar except for a small shift in the fluorescence spectrum of cationic toward longer wavelengths since their principal chromophores are identical. Though zwitterion and cationic have same chromophore, the absorption and emission maxima, fluorescence quantum yields, fluorescence lifetimes and nonradiative rate constants are different. These differences have been interpreted by the molecular structure.

2. The adding of strong acid to the dye solution showed the highest absorbance spectrum at concentration (10^{-3}) M with quenching in fluorescence spectrum, while the highest fluorescence spectrum and largest value of quantum efficiency for the dye solution were obtained by adding the strong base at concentration (10^{-5}) M and thus can be used in a wide range such as the active laser medium. For the weak acid and base, the absorption and fluorescence spectra were close to the dye solution spectrum for all concentrations, so the quantum efficiency values for them was also close.

3. Increasing the linear optical parameters (α_o, n_o, k, ε_{real}, ε_{im}) of the dye solution with increasing concentration, in addition to a decreasing in the optical energy gap for the allowed and forbidden indirect transitions. The largest value of (α_o, n_o, k, ε_{real}, ε_{im}) for the dye solution was obtained when adding the strong acid at concentration (10^{-3}) M, while it has the lowest value with the strong base at concentration (10^{-5}) M which shows the largest value for the optical energy gap.

4. The experimental data of nonlinear optical properties of two molecular forms of RhB dye solution at different concentrations show the displayed self-defocusing phenomena and a negative nonlinear refractive index, as well as a two-photon absorption coefficient, indicating that the sample could be useful in nonlinear optical devices.
5. The nonlinear optical parameters (n_2 , β) of the dye solution increase with increasing concentration. The largest value of nonlinear absorption coefficient of the dye solution was obtained by adding the strong base at concentration (10^{-3}) M, while it show highest value of nonlinear refractive index at the same concentration with the strong acid.

4.6 The Suggestions and Future Works

In this context, a further investigation can be suggested as future works:

1. Studying the linear and nonlinear optical properties of RhB dye as a solution and solid samples with different solvents.
2. Studying the nonlinear optical properties of RhB dye by using Z-Scan technique at different powers laser.
3. Studying the linear and nonlinear optical properties for lactone form of RhB dye by using Z-Scan technique with different solvents.
4. Studying the optical limiting behavior for three forms of RhB dye with different solvents.

Scientific Activities

1. Papers

a. Paper (Linear Optical Characterization of Rhodamine B and Malachite Green Organic Laser Dyes Mixture Solutions) has been accepted for publication in scopus container (Materials Science Forum).

b. Paper (Study Nonlinear Optical Properties of Two Molecular forms of Rhodamine B Dye Solution) has been accepted for publication in scopus container (Key Engineering Materials).

2. Conferences

Certificate of attendance in three international conferences and one national conference.

3. symposiums

Participation in two scientific symposium for postgraduate student in the faculty of science, department of physics, in addition to obtaining a certificate of attendance in eleven scientific symposiums.

4. training courses

Certificate of participation in five national training courses

5. electronic seminars

Participation in three electronic seminars in the department of physics, the most important of which was how to raise the level of scientific research among graduate students, as well as about the importance of publishing in international journals.

6. workshops

Certificate of attendance in three international and twenty-five national workshops.

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الخلاصة

تضمنت هذه الدراسة تحضير الشكل الحامضي لصبغة الرودامين B المذابة في مذيب الميثانول بتراكيز مختلفة 10^{-3}, 10^{-4}, 10^{-5} مولاري عند pH=1 . تم إجراء التحضير مرة بإضافة حامض الهيدروكلوريك القوي (HCl) ومرة أخرى بإضافة حامض الخليك الثلجي الضعيف (CH_3COOH) إلى محاليل الصبغة. تمت إضافة قاعدة هيدروكسيد الصوديوم (NaOH) وقاعدة الأمونيا (NH_3) إلى محاليل الصبغة للضبط على المدى pH=10 لتوليد الشكل القاعدي.

تمت دراسة الخصائص البصرية الخطية لمحلول صبغة الرودامين B قبل وبعد إضافة الحوامض والقواعد باستخدام مقياس امتصاص الطيف المرئي UV-Vis. أظهرت النتائج أن الخواص البصرية الخطية α_o ، n_o ، k تزداد بزيادة التراكيز، وجد أن أكبر قيم لهذه المعاملات هي 1.59 cm-1 ، 3.49 ، 7.16 والتي تم الحصول عليها باستخدام حمض الهيدروكلوريك بتركيز 10^{-3} مولاري.

وجد أن أكبر قيم لثوابت العزل الحقيقي والخيالي هي 12.24 و 5.01 على التوالي للشكل الحامضي الناتج عن اضافة الحامض القوي الى محلول الصبغة بتركيز 10^{-3} مولاري والذي يمتلك أدنى قيمة لفجوة الطاقة البصرية للانتقالات غير المباشرة المسموحة والممنوعة عند نفس التركيز.

تمت دراسة أطياف الفلورة لمحلول صبغة الرودامين B قبل وبعد الاضافة باستخدام مطياف الفلورة، لقد ثبت أن الكفاءة الكمية تزداد مع انخفاض التركيز لجميع المحاليل. تم رفع قيمة الكفاءة الكمية من 0.54 لمحلول الصبغة النقية بتركيز10^{-3} مولاري الى اكبر قيمة 0.91 للشكل القاعدي الناتج عن اضافة القاعدة القوية الى محلول الصبغة بتركيز 10^{-5} مولاري، يشير هذا إلى امكانية استخدامه كوسيط ليزري فعال. عند إضافة الحامض القوي إلى محلول الصبغة حدث كبت في أطياف الفلورة لمحلول الصبغة. بالمقارنة مع القاعدة القوية، فإن الكفاءة الكمية للحامض الضعيف والقاعدة الضعيفة المضافيين إلى محلول الصبغة زادت قليلاً جدًا.

تم دراسة الخواص البصرية اللاخطية باستخدام تقنية Z-Scan في حالتي الفتحة المفتوحة و الفتحة المغلقة للحصول على معامل الامتصاص اللاخطي (β) ومعامل الانكسار اللاخطي (n_2) على التوالي. تم اداء القياسات باستخدام ليزر الحالة الصلبة ذو الطول الموجي 457 نانومتر.

أظهرت النتائج زيادة المعاملات اللاخطية عند زيادة التراكيز لجميع المحاليل. وجد أن أكبر قيمة لمعامل الامتصاص اللاخطي كانت 0.156×10^{-3} cm/mW لمحلول الصبغة مع هيدروكسيد الصوديوم بتركيز 10^{-3} مولاري، وأكبر قيمة لمعامل الانكسار اللاخطي كانت 8.46×10^{-11} cm^2/mW لمحلول الصبغة مع حامض الهيدروكلوريك عند نفس التركيز.

تُظهر قياسات Z-Scan لشكلين جزيئيين لمحلول صبغة الرودامين B ظاهرة إلغاء التركيز الذاتي ومعامل الانكسار الغير خطي السالب في حالة الفتحة المغلقة، و امتصاص فوتونين في حالة الفتحة المفتوحة، مما يجعل هذه الصبغة مرشحًا جيدًا للاستخدام في العديد من التطبيقات البصرية غير الخطية مثل المحدد البصري.

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قسم الفيزياء

استخدام صبغة رودامين B كوسط ليزري فعال

أطروحة مقدمة إلى

مجلس كلية العلوم في جامعة بابل وهي جزء من متطلبات
نيل درجة دكتوراه فلسفة في الفيزياء

من قبل

شيماء جبار عبد الرزاق جبار

بكالوريوس علوم فيزياء ٢٠٠٧
ماجستير علوم فيزياء ٢٠١٠

بإشراف

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