The Linear Optical Properties of Rhodamin110 Organic Dye Doped with Metal Nanoparticles

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ABSTRACT

Background:
Laser dyes are unsaturated hydrocarbon compounds that have the advantage of having double or triple bonds coupled with carbon atom chains. This system benefits from light absorption in the visible range (200–700 nm) and the transmission spectrum of absorption in the visible range.

Materials and Methods:
This research has focused on the effect of adding ethanol solution to rhodamine110 dye with different concentrations, the linear properties (permeability, absorbance) of rhodamine110 dye were studied as it was dissolved in ethanol to prepare solutions with concentrations (0.01, 0.03, 0.05) and at room temperature.

Results:
The absorbance A of rhodamine110 dye with ethanol was calculated for the above concentrations, respectively, as well as the transmittance T was calculated for the above concentrations, respectively, to obtain curves and rhodamine110 dyes were mixed with nanomaterials to improve the properties of the dyes.

Conclusion:
In this study, according to Beer-Lambert's rule, increasing the dye concentration will increase absorbance, which will raise the linear optical coefficients (refractive index and coefficient of absorption) for all produced samples. The probability of electronic transitions will definitely be affected by the type of solvent, and this has an impact on linear optical characteristics, particularly the positions and width of the absorption spectra. And the addition of nanomaterials added better improvements to the dye. The results showed that the highest linear properties appeared when the silver nanomaterials with rhodamine110 dye.

Keywords:
Optical Properties, Nanoparticles, Rhodamine dye
1. INTRODUCTION

Organic laser dyes are high-molecular-weight luminous molecules with extensive conjugated double-bond systems. In a dye laser, these molecules are dispersed in an organic fluid. They frequently absorb a wide variety of wavelengths, ranging from ultraviolet to near-infrared [1]. The optical characteristics of materials may now be measured using a wide range of parameters, which have been developed throughout the years. Refractive index, also known as refractivity [2]. The ratio of refracted to incident intensity and absorbed to incident intensity is known as the absorption coefficient or absorbance [3]. Organic dyes have a broad absorption band in the visible region of the electromagnetic spectrum. This property can only be seen in organic compounds with long conjugated bond systems that alternate single and double bonds. The long-wavelength absorption bond of dyes is responsible for the change from the electronic to the absorption bond ground state S0 to the first excited singlet state S1. The ground state S0 of an absorption bond is produced by this process, which is frequently highly substantial. The transitional moment happens when oscillator strength is on the order of unity. The reversal process from S1 to S0 is what causes the spontaneous emission in dye lasers [4]. The size of a nanoparticle ranges from 1 to 100 nm. The unexpected physical and chemical behavior of matter at the nanoscale scale opens up a wide range of scientific applications, making nanoparticle research an exciting field of study. All attributes undergo significant modifications as particles shift from micro to nano size. For a given volume, materials at the nanoscale have a tremendous surface area. Surfaces and surface characteristics regulate several significant chemical and physical interactions [5]. The characteristics of a material with nanostructures can be significantly different from those of a substance with greater dimensions with the same composition [5]. N. Al-huda Talib studied the preparation of organic laser dyes doped with polymer and nano materials and the structural, spectral, linear and nonlinear optical properties. The linear optical properties for all prepared samples (solutions and thin films) have been studied, using UV-VIS spectra for different concentrations for each material dissolved in Dimethyl sulfoxide (DMSO) solvent [6]. S. F. Haddawi et al., showed plasmonic random lasing in two different dye types (Rh6G and RhB) at 1.5×10−5 concentrations when combined with Au, Ag, Au/Ag, and Au, Ag mixed NPs made by LAL at various concentrations. The scattering means free path and the lasing threshold were seen to decrease at high NP concentrations. Additionally, under the same conditions, Au NPs random lasing intensity was greater than Ag NPs, and their spike width was narrower [7]. J. Shymaa studied Rhodamine B dye as a laser- active medium. The result show increasing the linear optical parameters (αo and no) of the dye solution with increasing concentration [8]. José C. González-Crisostomo et al., studied potential photocatalysts for the removal of dyes were created by synthesizing nanoparticles of five photocatalytic systems based on pure zinc oxide and with rare earth ions M-ZnO (M = La3+, Ce3+, Pr3+, or Nd3+) calcined at 500 °C or 700 °C. ZnO's bandgap is reduced when rare earth ions are added, which makes it useful for enhancing photocatalytic capabilities [9]. Ilaria Fratoddi et al., Rhodamine B isothiocyanate-functionalized gold nanoparticles with an average diameter of 10 nm have been created. to explore the bonding between the dye molecules and the nanoparticles and understand the specifics of the aggregation caused by the interaction between dye molecules on various nanoparticles, the final material has undergone rigorous chemical and physical characterization [10]. In this work, we have synthesized the linear properties (permeability, absorbance) for the rhodamine 110 pure and grafted to nanoparticles (Au, Ag, Cu) dissolved in ethanol and methanal.
2. **THEORETICAL PART**

The observation of optical characteristics in materials is the outcome of the interplay of charge nature and distribution (molecular, electronic, or ionic) within a substance with electromagnetic radiation. When electromagnetic radiation strikes a material and interacts with it, a variety of processes take place. For example, some of the substance absorbs electromagnetic radiation, while other portions transmit through the material and are referred to as the transmitting ray and the reflected part, respectively.

The absorbance (A), also known as optical density, is a mathematical constant that connects a sample's particle density (concentration) and sample thickness (optical path length).

\[
A = \log \left( \frac{I_0}{I} \right) \tag{1}
\]

Where (I) represent the amount of light that enters the sample at the wavelength (the amount of light that is transmitted), and (I0) is the light's initial intensity (the light's incident intensity) before it is introduced into the sample. The equation can also be written

\[
I = I_0 e^{-\alpha_o P C_m L} \tag{2}
\]

Where \( \alpha_o P \): indicates for the coefficient of the optical absorption, \( L \) stands for the length of the optical path., and \( C_m \): stands for molar concentration. The equation is written.

\[
\ln \frac{I_0}{I} = \alpha_o P C_m L = A \tag{3}
\]

The proportion of incident light intensity (I) to transmitted light intensity (I0) is known as the transmittance of the medium. Additionally, it is capable of defining the radiation energy transferred through the medium for the radiation energy impacting it. It is provided via the relationship described below.

\[
T = \left( \frac{I_0}{I} \right) \tag{4}
\]

In accordance with the Beer-Lambert equation, the transmittance depends as the molar concentration (Cm) and optical path length (L) of the light are both increased. Regarding the medium's permeability, it is correlated with the solution (A)'s absorbance as stated in the equation.

\[
A = \log \left( \frac{I}{I_0} \right) = \log \left( \frac{I}{I_0} \right) = \log \left( \frac{I}{I_0} \right) \tag{5}
\]

This connection illustrates that the permeability (T) rises as the absorbance (A) of the medium decreases.
3. MATERIALS AND METHODS

Proteinases may be measured in solution or inside of live cells using the sensitive and focused substrate rhodamine 110. The wavelengths of excitation are 498 nm and the emission are 521 nm. Its chemical formula is (C20H15ClN2O3) with molecular weight Mw= 366.80 gm/mol.

![Chemical Structure of Rhodamine 110](image)

**Figure 1:** Chemical Structure of Rhodamine 110 [11]

This study used two organic solvents: ethanol (Ethyl Alcohol), having the chemical formula C2H5OH and a molecular weight of 46.04 gm/mol, [12]. The Rhodamine 110 solutions used in the present work were made by dissolving the dye powder (0.011) gm in a volume (30) ml of various solvents (ethanol), and the concentration was determined (1×10⁻³) using the equation following.

\[
W = c \times v \times M.w / 1000
\]  

(1)

Where:
- W: dye weight
- c: molar concentration mole/l
- M.w: weight of molecular
- v: solvent volume

The solutions prepared were diluted according to the \((C_1V_1 = C_2V_2)\)  

(2)

- C1: primary concentration
- C2: new concentration
- V1: the volume before dilution
- V2: the volume after dilution
Three concentrations were prepared for R110 are \([1 \times 10^{-5} \text{ mM}, 3 \times 10^{-5} \text{ mM}, 5 \times 10^{-5} \text{ mM,}]\)

**Figure 2**: Rh 110 dye samples in various concentrations in solutions within ethanol solvent.

### 3.1 Preparation of the Nanoparticles (NPS)

The core nanoparticles in liquid media were fabricated using laser ablation in the liquid method. The used materials are Au, Ag and Cu target (>99.99% purity, Sigma Aldrich, Germany) is a thickness of (1 mm). The liquid media used was ethanol. The experiments will be made by using Q-switched Nd: YAG lasers (QUANTEL–Brilliant, USA), operating at a wavelength (1064 nm), a pulse width of (5 ns), and repetition rate of (10 Hz), energy per pulse will focus on the samples. A colloidal solution of gold particles, silver particles, and copper particles was prepared with solvents ethanol using PLAL, by taking a gold bar, a silver bar, and a copper bar with a purity of 99.9% and placing it in a glass beaker containing distilled ethanol after cleaning the metal with alcohol to remove impurities. Then an Nd:YAG laser beam with wavelength (1064 nm) is projected onto the plate inside the enclosure through a convex lens (10 mm), and the necessary power was (120 mJ/pulse, pulse width 5 ns, 6 Hz, 30 nanoseconds) to complete the process of removing gold particles, silver particles, and copper particles. I noticed in the gold particles a change in the colour of the liquid to a dark red colour, which indicates the formation of the nanoliquid. In the silver particles, the colour of the liquid changed to a brownish-red solution, while the copper changed to a semi-transparent color. Figure (3) represents the device used for laser ablation and an experimental scheme for preparing nanoparticles. and Figure (4): the solutions samples of NPs dye in an Ethanol solvent.
3.2 Preparation of the (Rh 110 /Nps) nanocomposite solutions

The nanocomposite is prepared by taking (1ml) of the colloidal solution of gold, silver and copper nanoparticles dissolved in ethanol solution and adding it to the (Rh110) and stirring it by magnetic stirring for (30 minutes), thus obtaining the (Rh 110 - NPs) nanocomposite. Figure (5) shows the solutions samples of (Rh 110 - NPs) nanocomposite at various concentrations in ethanol solvent.
3.3 Transmission Electron Microscope (TEM)

Transmission electron microscopy (PHILIPS, CM 120) is used to examine the morphology of (NPs). TEM is a technique of microscopy in which an electron beam is transmitted through a specimen to form an image. An image is formed from the electrons’ interaction with the sample as the beam is transmitted via the specimen. The image is then magnified and centred on an imaging device like a fluorescent tube, a photographic film plate, or a sensor like a scintillator connected to a load-coupled device. Figure (6) presents the TEM device.
4. RESULTS AND DISCUSSION

4.1 The Results of TEM Images

TEM was performed to investigate the core size and shape of the (NPs). Figure 7 includes images representing the nanoparticles (Au, Ag and Cu) with (50) nm and (100) nm magnification power. TEM results show spherical and well-dispersed nanoparticles. In general, the nanoparticles are isotropic in shape. From the TEM photos, it can be concluded that all the (NPs) present with spherical morphology Figure (6): shows TEM images of (a) Ag in Ethanol, (b) Au in Ethanol (c) Cu in Ethanol.

Figure 7: TEM image of (a) Ag in Ethanol, (b) Au in Ethanol (c) Cu in Ethanol

4.2 The Results of linear optical properties

Figure (8 a) shows the absorbance spectra of Rhodamine110 dye solutions dissolved in ethanol solvent at different concentrations (0.01, 0.03,0.05) M, which were measured using spectrometers of visible and ultraviolet rays. It is noted from the figure that increasing the concentration leads to an increase in the absorbance values, and this is consistent with the law Pierre-Lambert. From the results of the absorbance spectra, the transmittance spectra were calculated, as Figure (8.b shows the spectra of the permeability of these solutions, and it is noted from this figure the decrease in the permeability values with increasing concentration . From the results of the absorbance and transmittance spectra, the values of the linear refractive index (no) and the linear absorption coefficient (αo) were calculated. Table (1) shows the most important linear optical properties of
Rhodamine110 dye solutions at the wavelength value (532 nm), and it is noted from the table that the values of the coefficients Optical linearity increases with increasing concentration due to the increase in absorbance value.

Figure 8: The spectra of a. Absorbance for R110 dye solutions dissolved in ethanol solvent with different concentrations. b. The spectra of transmittance for R110 dye solutions dissolved in ethanol solvent with different concentrations.

Table 1: The linear optical properties of R110 dye dissolved in ethanol solvent.

<table>
<thead>
<tr>
<th>C (M)</th>
<th>A</th>
<th>T</th>
<th>α₀</th>
<th>n₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.07</td>
<td>0.84</td>
<td>0.17</td>
<td>1.37</td>
</tr>
<tr>
<td>0.03</td>
<td>0.18</td>
<td>0.66</td>
<td>0.42</td>
<td>1.84</td>
</tr>
<tr>
<td>0.05</td>
<td>0.26</td>
<td>0.54</td>
<td>0.60</td>
<td>2.06</td>
</tr>
</tbody>
</table>

While in the Figure 9 show the absorption intensity of R110/Nps The influence of the method of pulsed laser ablation in liquids on the concentrations prepared from the dye was recorded, and it was noted that numerous possibilities arise in the addition process. One of these effects is a shift in wavelengths either in the direction of (redshift) or in the direction of (blue shift) when the quantity of nanoparticles inside the liquid increases (blue shift) this is dependent on the particle size of the nanoparticles that have been created. The intensity of absorption is the other impact, in which the concentration of the chemical is linked to an increase or reduction in absorption. When the size of the produced nanoparticles is tiny and added to the dye, the intensity of absorption decreases as the dye concentration decreases. Table 2 shows the values of coefficient of linear absorption, and linear refractive index of (R110/NPs) nanocomposite solutions dissolved in ethanol solvent. By comparing the results, we notice that the highest absorbance was obtained when mixing R110 with AgNps,
which is much higher than that of the pure dye. Thus, the addition of nanomaterials to the dye R110 gave much better results.

![Graph](image)

**Figure 9**: The spectra of Absorbance and transmittance for (R110\Nps) blend solutions dissolved in ethanol solvent

**Table 2**: The linear optical properties of (R110/NPs) nanocomposite solutions dissolved in ethanol solvent

<table>
<thead>
<tr>
<th>[Dye+NPs]</th>
<th>α</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh110 Pure</td>
<td>0.06</td>
<td>2.06</td>
</tr>
<tr>
<td>Rh110+CuNPs</td>
<td>0.69</td>
<td>2.12</td>
</tr>
<tr>
<td>Rh110+AuNPs</td>
<td>0.81</td>
<td>2.15</td>
</tr>
<tr>
<td>Rh110+AgNPs</td>
<td>0.89</td>
<td>2.18</td>
</tr>
</tbody>
</table>

5. **CONCLUSIONS**

In this study, according to the Beer-Lambert rule, increasing the dye concentration will lead to an increase in the absorbance, which will raise the linear optical coefficients (refractive index and absorption coefficient) for all the samples produced. The potential for electronic transitions will certainly be affected by the type of solvent, and this has an impact on the linear optical properties, particularly the positions and widths of the absorption spectra. Since methanol has a stronger polarity than ethanol. And the addition of nanomaterials added better improvements to the dye. The results also showed the possibility of using all models of pure and doped dyes with nanomaterials as potential media for various photovoltaic applications as optical energy limiters and as effective laser mediators in liquid lasers.
Conflict of interests
There are non-conflicts of interest.

References
الخلاصة

المقدمة:
أصبغ الليزر عبارة عن مركبات هيدروكربونية غير مشبعة تتميز بوجود رواسب مختلفة أو ثلاثية مفيدة بسلاسل ذرات الكربون. ينتمي هذا النظام من امتصاص الضوء في النطاق المرئي (200–700 نانومتر) وطيف النافذة للامتصاص في النطاق المميز.

طرق العمل:
ركز هذا البحث على تأثير إضافة محلول الإيثانول إلى صبغة رودامين 110 بتركيزات مختلفة ودُرست الخواص الخطية (النافذة، الامتصاصية) لصبغة رودامين 110 حيث تم إذابتها في الإيثانول لتحضير المحاليل بتركيزات (0.01 – 0.03 – 0.05) ودَرست الخواص الخطية في درجة حرارة الغرفة.

النتائج:
تم حساب الامتصاصية A لصبغة رودامين 110 مع الإيثانول للتركيزات المذكورة أعلاه ، على التوالي ، وكذلك تم حساب النافذة T للتركيزات المذكورة أعلاه ، على التوالي ، للحصول على منحنى A للنافذة، وتم خلط صبغة رودامين 110 مع مواد نانوية لتحسين خصائص الأصباغ.

الاستنتاجات:
في هذه الدراسة ، وفقا لقاعدة Beer–Lambert في هذه الدراسة ، فإن زيادة تركيز الصبغة سيزيد من الامتصاصية ، مما سيرفع المعاملات البصرية الخطية (معامل الانتشار ومعامل الامتصاص) لجميع العينات. من المعركة أن احتمالية التحول الإلكترونية ستتأثر بنوع المذيب ، وهذا له تأثير على الخصائص البصرية الخطية ، لا سيما مواضع تأثير أطياف الامتصاص. وإضافة المواد النانوية أضافت تحسينات أشياء أفضل للصبغة. أظهرت النتائج أن أعلى الخواص الخطية ظهرت عند صبغ اللفة مع صبغة رودامين 110.

الكلمات المفتاحية:
الخصائص البصرية , الجسيمات النانوية , صبغة الرودامين

الخصائص البصرية , الجسيمات النانوية , صبغة الرودامين