Research Article GU J Sci 34(2): 550-560 (2021) DOI:10.35378 /gujs.666716

Gazi University

Journal of Science

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Estimation of Theoretical Models of Photophysical Processes for Fluorescein Laser Dye with Ag Nanoparticles

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Highlights

- This paper focuses on estimation of theoretical models of photophysical processes.
- A novel theoretical method is proposed for the absorption and fluorescence spectral estimations.
- An excellent matching profiles based on Logistic Power Peak (LPP) function were obtained.

Article Info

Received: 28 Dec 2019
Accepted:27 Oct 2020

Keywords

Logistic power peak
Fluorescein dye
Ag nanoparticles
FRET
Theoretical model

Abstract

In this study, a novel theoretical method for the absorption and fluorescence spectral estimations has been presented. These estimations have been based on experimental measurements of absorption and fluorescence spectra for the solutions of Fluorescein laser dye with Silver (Ag) nanoparticles in distilled water. The used concentration was ($1x10^{-5}$ M) for Fluorescein dye, while the mass amounts were (0.003g, 0.005g, 0.0065g, 0.008g and 0.0085g) for Silver nanoparticles. A spectral absorption enhancement was detected in the case of increased Silver nanoparticle masses, which specify that the doped Fluorescein dye with Ag nanoparticles has an important effect on the dye absorption spectra. On the other hand, each fluorescence emission spectrum for the dye has quenched as Ag nanoparticle's mass amounts have increased. The related amounts of mass increase as a consequence of Förster resonance energy transfer (FRET). The novel approach of theoretical estimations has been based on curve fitting using Logistic Power Peak (LPP) function to estimate theoretical models for the absorption and fluorescence spectra of these samples. These rated models have excellent matching profiles with the experimental profiles so that the estimated models can replace the experimental measurements.

1. INTRODUCTION

In recent years, significant efforts have been made for the spectral investigations of absorption and fluorescence emissions of xanthene laser dyes, especially Fluorescein, and doping them with metal and non-metal nanoparticles. These investigations of laser dyes are due to their unique and significant properties as well as their performance for biological and medical applications. Chubinidze, et al. [1], demonstrated that doping organic dyes with gold nanoparticles can enhance the luminescent intensity of these dye, which can be used for diagnosis and therapy of cancer. Wang, et al. [2], highlighted the uses of fluorescein dye for detecting and bio-imaging applications in vitro and in vivo. Amador-Patarroyo, et al. [3], studied the effect of using Fluorescein on the imaging of tomography and angiography. Ge, et al. [4], showed the medical applications of silver nanoparticles. Laser dyes doped with nanoparticles can be used also for inspecting the optical properties of scattering media as in laser action [5, 6]. In 2012, Al-Kadhemy, et al. [7], studied the absorption spectra of Styrene-butadiene in Toluene using the Table curve 2D program, which initiates the using curve fitting software in the spectral calculations. Quenching of the fluorescence by FRET has examined for nanoparticles with xanthene dyes by Zeinidenov, et al. [8], and by Barzan and Hajiesmaeilbaigi [9]. They stated that at short distances and direct contact between nanoparticles and

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xanthene dyes, the fluorescence will be quenched as a result of the FRET from fluorescent molecules to nanoparticles.

The objective of this study is to create a new approach for estimating theoretical models of the spectral behavior of the Fluorescein dye with Ag nanoparticles. These estimated models have been made based on experimental measurements of absorption and fluorescence spectra of Fluorescein dye with Ag nanoparticles along with the different amounts of mass. The curve fitting process had made using Table curve 2D software to estimate theoretical models for the spectra of absorption and fluorescence. The estimated theoretical models are based on Logistic Power Peak (LPP) function. This function has been used for numerous purposes in estimating soil properties [10] and light-emitting diode (LED) spectral calculations [11]. Furthermore, it can be seen from the limited works on using LPP function, there is no attempt was done to explore the potential of this function for estimating theoretical models of the spectral behavior of the laser dyes. Nevertheless, the uniqueness of this study exists in the fact that this is the first time to use (LPP) function in estimating theoretical models of the spectral profiles of the Fluorescein dye with Ag nanoparticles.

2. MATERIAL METHOD

In this experiments, the sample medium with a suspension has 0.003g, 0.005g, 0.0065g, 0.008g and 0.0085g of Ag nanoparticles with an average diameter of 50 nm and purity of 99.99% to be processed with Fluorescein dye ($C_{20}H_{12}O_5$, BDH, M_W=332.306 g/mol) and 10 ml of distilled water. The solution of dye sample with a concentration of ($1x10^{-5}$ M) has prepared using the following equation [12]:

$$m = C\ V\ Mw \tag{1}$$

where m is the amount of dye needed to obtain the desired concentration, C is the required concentration of dye, V is the volume of solvent for the dye, and Mw is the molecular weight of dye. The dye chemical structure is depicted in Figure 1.

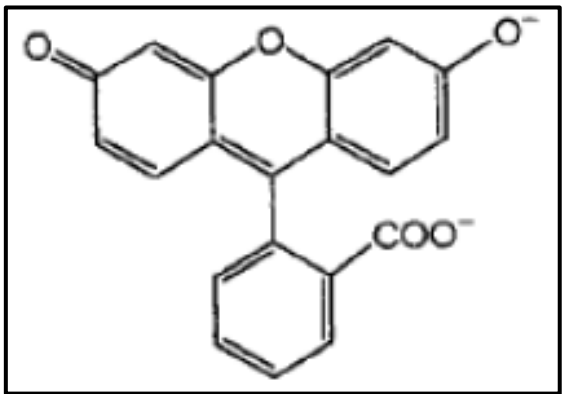

Figure 1. *Chemical structure of Fluorescein laser dye [12]*

All used samples have prepared with hot plate stirrer until the Ag nanoparticles regularly distributed through the Fluorescein dye solution at room temperature (30ºC). Also, all spectrums of absorption and fluorescence have been measured by a UV-visible spectrophotometer (T70/T80) and spectro-fluoro-photometer (SHIMADZU RF-5301pc), respectively.

The crystalline structure of Ag nanoparticles has been confirmed by X-ray diffraction (XRD) using SHIMADZU XRD – 6000, Cu Kα, under 2θ range of 10 to 80º.

The measured XRD pattern of Ag nanoparticles has shown in Figure 2. The pattern explains that the Ag nanoparticles are in a crystalline cubic system with a lattice constant of a = 4.0860 Å. Strong diffraction peaks are at 38.1º (111), 44.2º (200), and 64.4º (220).

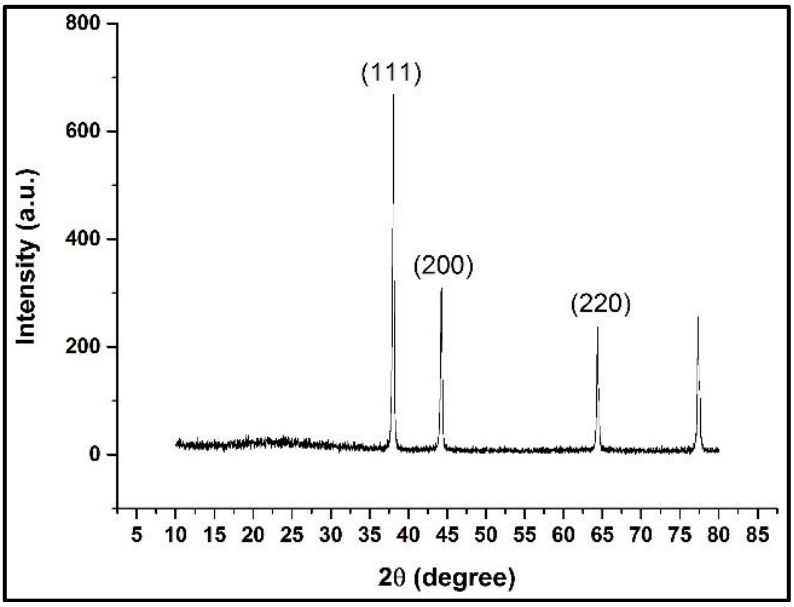

***Figure 2**. Measured XRD pattern of Ag nanoparticles*

3. EXPERIMENTAL DETAILS

3.1. Absorption and Fluorescence Spectra

The spectra of absorption and fluorescence for Fluorescein dye (F) with a concentration of (1 x10^{-5} M) with and without Ag nanoparticles of (0.003g, 0.005g, 0.0065g, 0.008g, and 0.0085g), are presented in Figure 3. The highest peak of the absorption is at (λ_e= 490 nm), while the highest peak for fluorescence is at (λ_f= 514 nm) for Fluorescein laser dye. All details of these results are depicted in Table 1.

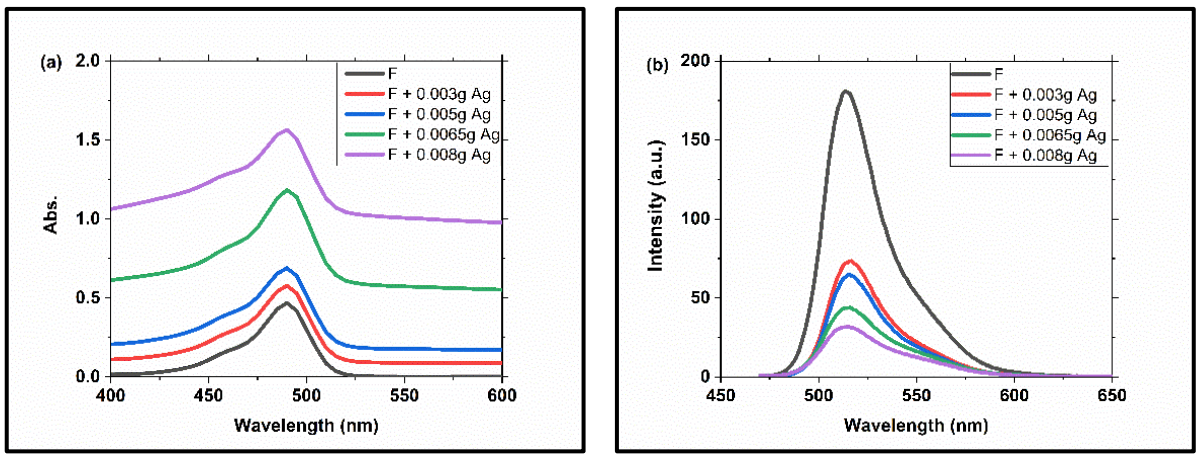

***Figure 3.** Absorption (a) and fluorescence (b) spectra of Fluorescein (F) with different amounts of mass of Ag nanoparticles*

Table 1. *Fluorescein dye with different amounts of mass of Ag nanoparticle*

Dyes	Ag (g)	λ_e (nm)	Absorption Intensity	λ_f (nm)	Fluorescence Intensity
F ($1x10^{-5}$M)	0	490	0.468	514	180.82
	0.003	490	0.578	517	73.44
	0.005	490	0.689	516	64.66
	0.0065	490	1.184	516	43.85
	0.008	490	1.565	515	31.86

Figure 3 and Table 1 show, it is comprehensible that by intensifying Ag nanoparticle mass amount, the absorption spectra will be proportionally enhanced. In contrast, a dynamic quenching process becomes principal, and fluorescence intensities decrease down instantaneously. This behavior can be explained by the Förster resonance energy transfer (FRET) mechanism between Fluorescein laser dye (as a donor) and Ag nanoparticle (as acceptor). The FRET quenching from the present study agrees relatively well with that from Zeinidenov, et al. [8], and Barzan and Hajiesmaeilbaigi [9]. Moreover, there is a small redshift in the fluorescence intensity with increasing Ag nanoparticle amounts of the mass. Adding (Ag) nanoparticles as scattering particles to the dye solution can cause more collisions (random walk) between light and these particles, which means more loss of energy, thus, longer wavelengths for emitted photons (red shift).

3.2. Theoretical Estimation of Absorption and Fluorescence Spectra

A theoretical estimation for absorption and experimental fluorescence spectra of a single concentration of dye with varied amounts of the nanoparticles masses achieved using Table curve 2D software. A curve fitting process applied for curves in Figure 3, where the results are presented in Figures 4 and 6. This gives idea to find a suitable one curve fitting equation that can be used for these spectrums. The adopted curve fitting equation in this study is a different kind of Gaussian function. This kind is called Logistic Power Peak (LPP). The mathematical description of this function is given by:

$$Y=\frac{a+b}{e}\left(1+\exp\left(\frac{x+d\ln(e)-c}{d}\right)\right)^{\frac{-e-1}{e}}\exp\left(\frac{x+d\ln(e)-c}{d}\right)(e+1)^{\frac{e+1}{e}} \quad (2)$$

for $e \geq 1$, $d \neq 0$.

Where *a* and *b* are stand for the minimum and maximum values of the amplitude, *d* is the width of the spectrum over time, *c* is the highest position, and *e* is the symmetry around the peak ($e = 1$) or not ($e > 1$). The equation of theoretical estimation has been studied for other values of Ag nanoparticle masses, which have not taken experimentally with Fluorescein dye solution in distilled water through concentration of ($1x10^{-5}$ M).

The fitting curves of Figure 3 of absorption illustrated in Figure 4, while Figure 5 shows and the parameters for all concentrations. Figures 6 and 7 clarify the fitting curves and their parameters for experimental fluorescence spectra for Fluorescein dye solution with Ag nanoparticles.

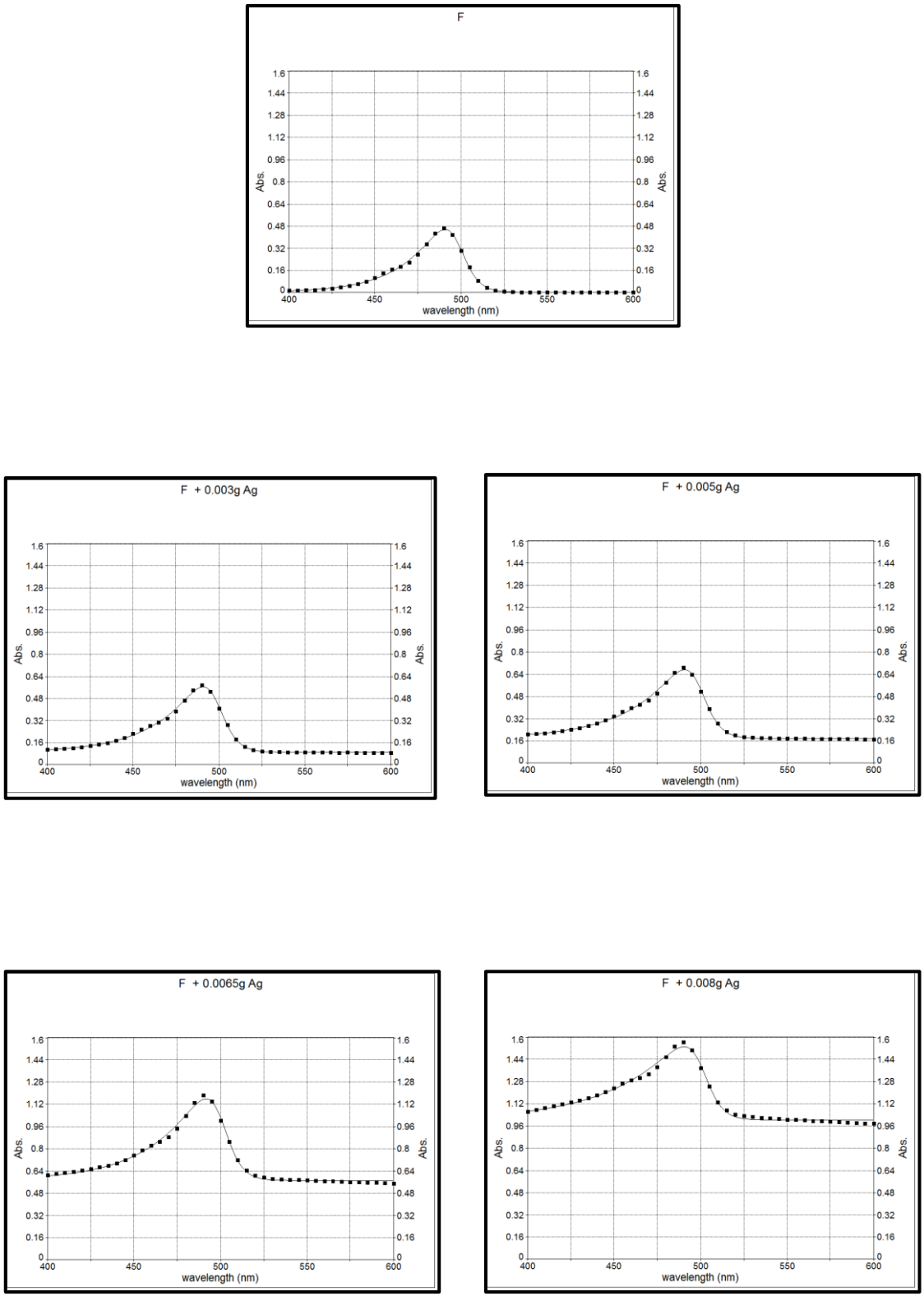

Figure 4. *Curve fitting of absorption spectra for Fluorescein with Ag nanoparticles*

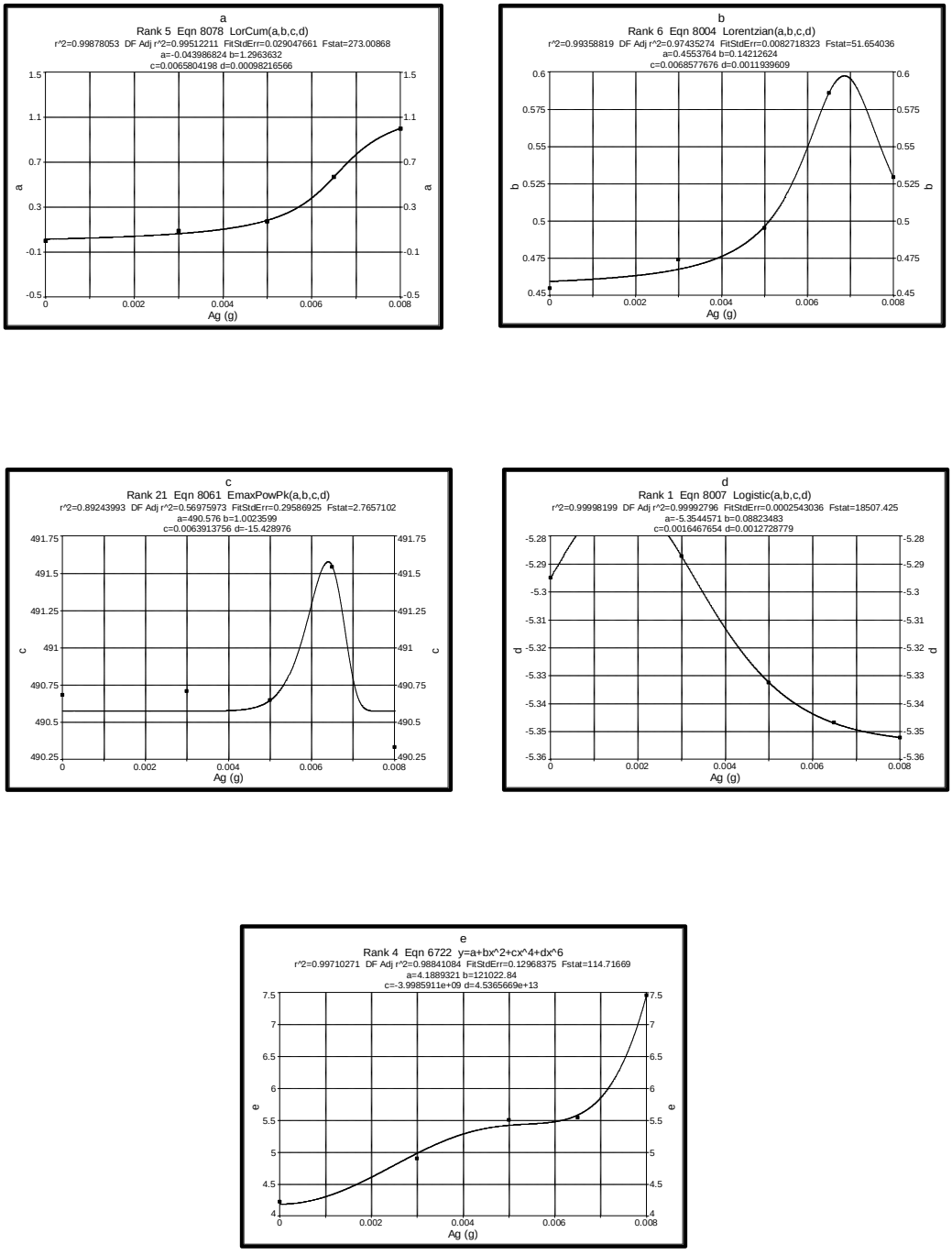

Figure 5. *The parameters of Figure 4 to Fluorescein with Ag nanoparticles for absorption spectra*

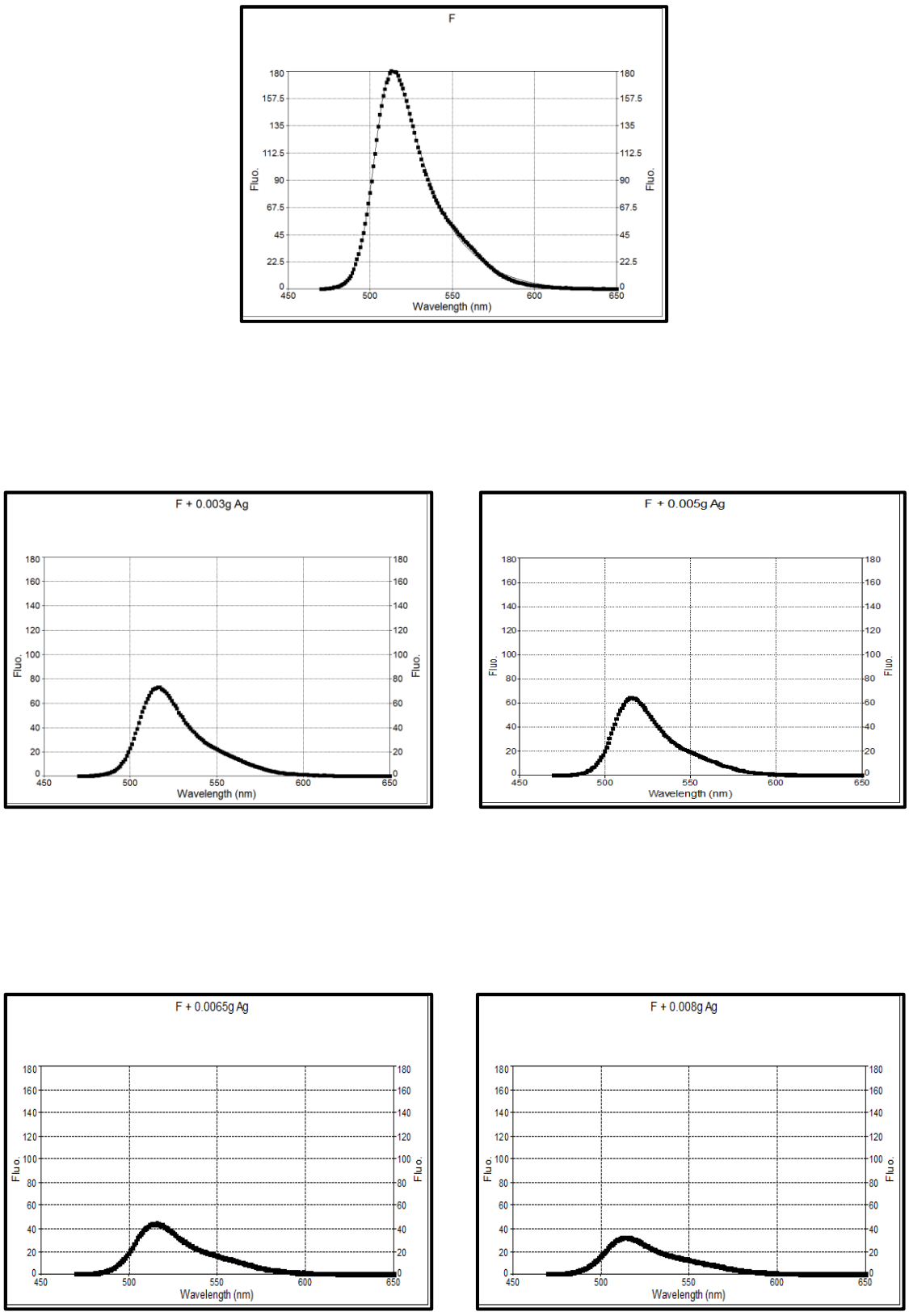

Figure 6. *Curve fitting of fluorescence spectra for Fluorescein with Ag nanoparticles*

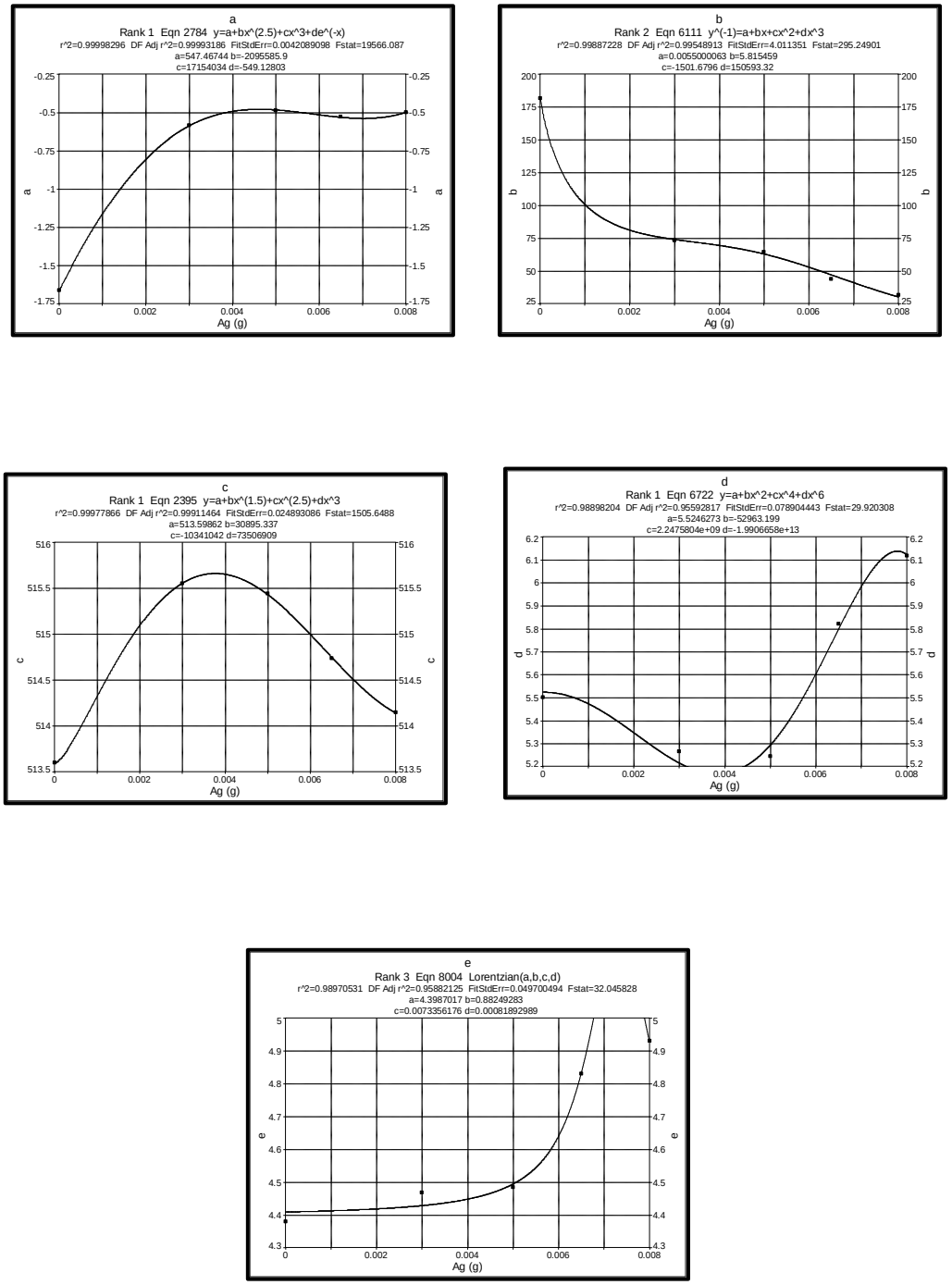

Figure 7. *The parameters for Figure 6 of Fluorescein with Ag nanoparticles for fluorescence spectra*

The curve fitting parameters from Figures 5 and 7 have been summarized in Tables 2 and 3, which contain the absorption and fluorescence parameters of experimental and theoretical values (referred by theo) of Ag nanoparticle masses with Fluorescein dye. The parameter (r^2) is the correlation coefficient used to measure the relationship level between two variables, in this work the two variables are the experimental parameters and theoretical estimated curve fitting profiles.

Table 2. *Parameters of Fluorescein with Ag nanoparticles for absorption spectra*

Ag (g)	a	b	c	d	e	r^2
0	0.0019645	0.4547493	490.6841	-5.2948479	4.2251472	0.9972
0.002 Theo	0.0431	0.4634	490.576	-5.2678	4.6119	
0.003	0.0895834	0.474308	490.70927	-5.2870996	4.9036548	0.9975
0.004 Theo	0.106	0.4764	490.5789	-5.3129	5.2874	
0.005	0.1766328	0.4952207	490.6481	-5.3324943	5.5060997	0.9973
0.0065	0.5717903	0.5859673	491.54438	-5.3467926	5.5440368	0.9947
0.007 Theo	0.7707	0.5955	490.7871	-5.3493	5.8556	
0.008	1.0022411	0.5294115	490.33495	-5.3522162	7.4558814	0.9918

Table 3. *Parameters of Fluorescein with Ag nanoparticles for fluorescence spectra*

Ag (g)	a	b	c	d	e	r^2
0	-1.6608078	181.82968	513.60057	5.5025927	4.3808979	0.9988
0.002 Theo	-0.801	81.1098	515.1	5.3474	4.419	
0.003	-0.5841514	73.553688	515.55313	5.2664076	4.4682154	0.9988
0.004 Theo	-0.4911	69.5751	515.6546	5.171	4.4488	
0.005	-0.4850529	64.621258	515.44728	5.2444261	4.4844449	0.9988
0.0065	-0.5276007	43.846555	514.73705	5.8231003	4.831586	0.9974
0.007 Theo	-0.5374	41.1871	514.5112	5.9838	5.1542	
0.008	-0.4987513	31.855838	514.14931	6.1181711	4.9307961	0.9965

To further investigate the estimated theoretical models of absorption and fluorescence spectra, a profile containing the hypothetical values of Ag nanoparticle masses with Fluorescein dye has been achieved as explained by Figure 8, where the fluorescein dye (F) without any addition of (Ag) nanoparticles is the reference data.

The behavior of theoretical absorption and fluorescence spectra has been similar to the behavior of experimental spectra in Figure 3. Accordingly, the theoretical models based on the used curve fitting equation in Equation (2), have given a high matching with the experimental results.

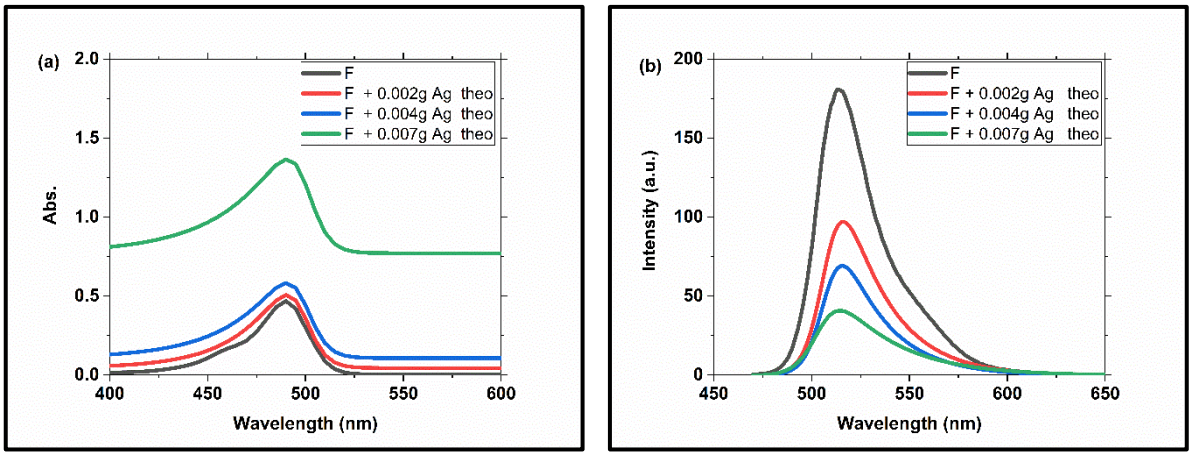

Figure 8. *Theoretical absorption (a) and fluorescence (b) spectra for Fluorescein with Ag nanoparticles*

For comparison, all experimental and theoretical results (referred by theo) of Ag nanoparticles with Fluorescein dye have listed in Table 4.

Table 4. *Fluorescein dye with different amounts of mass of Ag nanoparticles*

	Ag (g)	λ_e (nm)	Absorption Intensity	λ_f (nm)	Fluorescence intensity
F ($1x10^{-5}$ M)	0	490	0.468	514	180.82
	0.002 Theo	490	0.506	516	96.984
	0.003	490	0.578	517	73.44
	0.004 Theo	490	0.581	516	69.055
	0.005	490	0.689	516	64.66
	0.005 Theo	490	0.841	515	54.456
	0.0065	490	1.184	516	43.85
	0.007 Theo	495	1.365	515	40.627
	0.008	490	1.565	515	31.86

4. CONCLUSIONS

The present study was designed to find a novel theoretical estimation for experimental absorption and fluorescence spectra of single concentration samples of Fluorescein dye with variable Ag nanoparticle masses. This study has shown that the best-fitting equation for these samples was the Logistic Power Peak (LPP) equation, in absorption and fluorescence spectra. The behavior comparison of the theoretical and practical spectral profiles can make the estimated models an excellent replacement for the experimental measurements, which can save the time, cost and availability of the measuring devices. Furthermore, the findings of this study suggest that the estimated models can give an acceptable presumption of the overall spectral behaviors of doped Ag nanoparticles with Fluorescein laser dye.

ACKNOWLEDGMENTS

The authors would like to thank Mustansiriyah University (www.uomustansiriyah.edu.iq) Baghdad-Iraq for its support in the present work.

CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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