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Study the optical properties of Fluorescein sodium dye doped in polymer Poly Polyvinyl alcohol for different thickness

دراسة الخواص البصرية لصبغة فلورسين الصوديوم المطعمة بالبوليمر بولي فنيال الكحول للأسماك المختلفة

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ABSTRACT

Z-scan method has been utilized at (532nm) and uv-visible and fluorescence spectrophotometer have been utilized to study the spectral characteristics in order to compute the nonlinear optical properties in two cases close, open aperture. The refractive index n_2 and absorption coefficient β of various thicknesses (4,6,8,10,12) μm for constant concentration (5×10^{-2} M) have been determined. The empirical results for open- aperture showed that the film models of fluorescein sodium dye have shown the saturation absorption or the two photon absorption, also in closed-aperture showed positive or negative effect. Likewise for thicknesses quantum efficiency have been calculated.

Keywords: Fluorescein sodium , linear and non-linear optical properties, Z-Scan method, Fluorescence quantum efficiency.

الخلاصة

تم استخدام تقنية المسح على المحور الثالث عند الطول الموجي 532 نانوميتر وجهازا قياس الامتصاصية والفلورة لحساب الخصائص الطيفية، تم استخدام التقنية لحساب الخواص البصرية اللاخطية في حالتين الفتحة المغلقة والفتحة المفتوحة المتمثلة بمعامل الانكسار اللاخطي ومعامل الامتصاص اللاخطي للأسماك المختلفة (4,6,8,10,12) مايكروميتر للتركيز الثابت (5×10^{-2}) مولاري. واظهرت النتائج العملية للفتحة المفتوحة ان نماذج الافلام لصبغة فلورسين الصوديوم تظهر سلوك امتصاص مشبع اوامتصاص فوتونين ، وايضا للفتحة المغلقة اظهرت تاثير موجب او سالب. كذلك تم حساب الكفاءة الكمية للأسماك المذكورة.

1.INTRODUCTION:

Z-scan method was created by Mansoor Sheik-Bahae et.al [1,2] because of simplicity and high sensitivity were utilized for determining the nonlinear optical properties for various materials [3]. Non-linear optics are imperative parameters because of their applications to many branches that occurred from the interaction between beam of light and matter [4,5,6,7]. The empirical part computed when the film model is moved along Z-axis through the beam waist of Gaussian beam of laser gradually. In figure (1) (2) two sorts of Z-scan method to compute n_2 and β respectively [2].

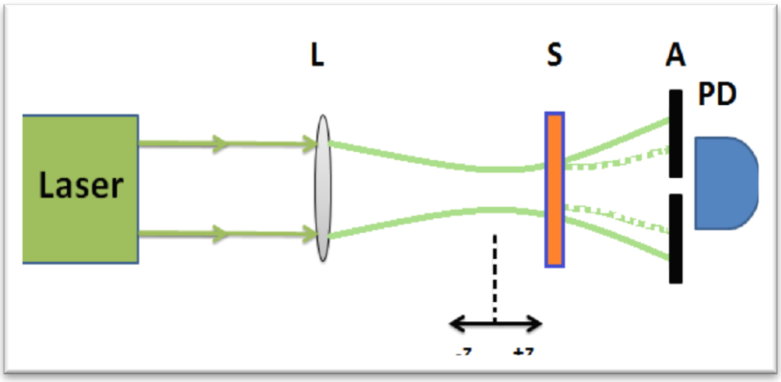

Figure (1): schematic drawing close-aperture.

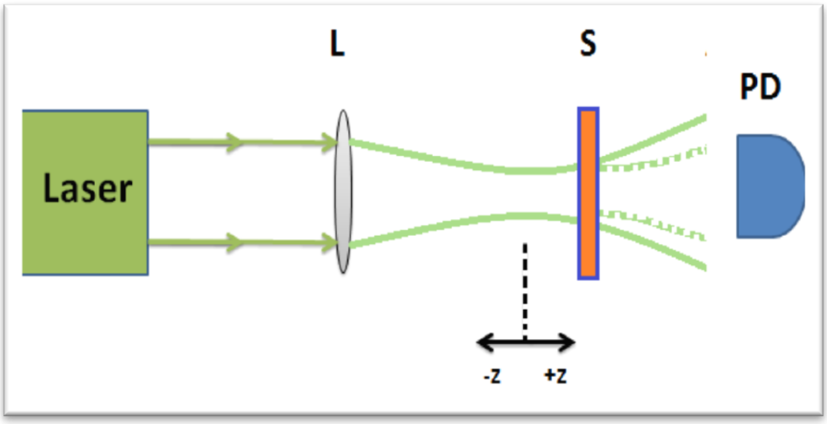

Figure (2): schematic drawing open-aperture.

Xanthene dye is important dye, it have strong optical absorption, long phosphorescence life time and number of double bonds. Fluorescein Sodium dye was a typical material utilized as a medium described by high chemical stability, efficient manufacturing, has a chemical formula of ($C_{20}H_{10}Na_2O_5$) and Molecular weight (376.3 $\frac{g}{mol}$), orange- red powder was dissolved in alcohol [8]. Figure (3) demonstrated the molecular structure of dye.

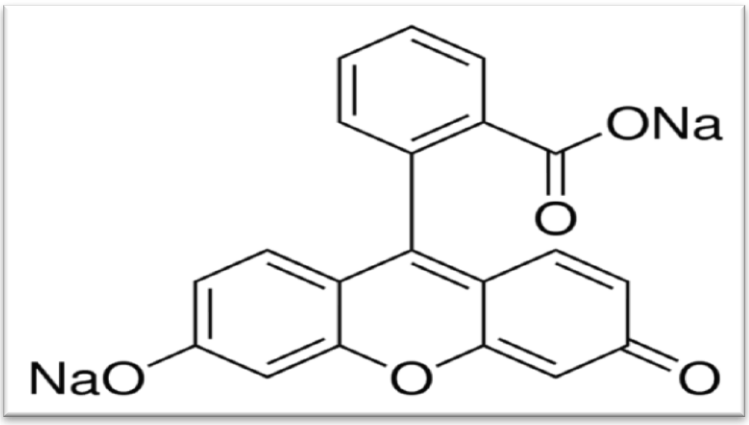

Figure (3): The structure of Fluorescein sodium[9].

2.METHODOLOGY

2.1. Fluorescence Quantum Efficiency

fluorescence quantum efficiency (q_{FM}) can be defined as the proportion of the number of quanta emitted to the number of quanta absorbed. The molecular fluorescence spectrum F($\bar{\upsilon}$) is then characterized as the relative fluorescence quantum intensity at frequency ($\bar{\upsilon}$) ,normalized by the relation[10].

$$q_{FM} = \frac{\text{Number of emitted photons}}{\text{Number of absorbed photons}} \ldots\ldots\ldots\ldots\ldots (1)$$

$$= \frac{K_{FM}\,[M^*]}{I_a}$$

K_{FM} : is the rate of fluorescence emission.
M^*: is the molar concentration of excited molecules.
I_α: is the intensity of light absorbed.
quantum efficiency can be ascertained by the total area under the fluorescence curve, depending on the equation[11].

$$q_{fm} = \int_0^\infty F(\bar{\upsilon})\,d\bar{\upsilon} \ldots\ldots\ldots\ldots\ldots (2)$$

$F(\bar{\upsilon})$: is the intensity of fluorescence spectrum.
Quantum efficiency was considered as the most essential parameter of the dye molecular, and its values range between (0-1), depend on nature concentration, viscosity, temperature and the solvent molecular structure nature[12].

2.2. Fluorescein sodium

Fluorescein Sodium (FS) dye is used in this present work. The properties of this dye were displayed at table (1).

Table (1) : The principle qualities of FS dye.

Productive company	Lambda physics (Germany)
Molecular formula	$C_{20}H_{10}Na_2O_5$
Molecular weight	376.27 $\frac{g}{mol}$
Solvent	Ethanol
Appearance	Orange -red to dark red crystalline powder

2.3. Polyvinyl alcohol

It is a white powder which has numerous properties like effectively fabricated, relative minimal cost, good charge storage and dielectric material[13]. The properties of this polymer were displayed in table (2) and the PVA molecule was clarified in figure (4).

Table (2) : The principle qualities of polymer.

Molecular formula	C_2H_4O
Solubility	Water soluble
Physical Appearance	White, odorless

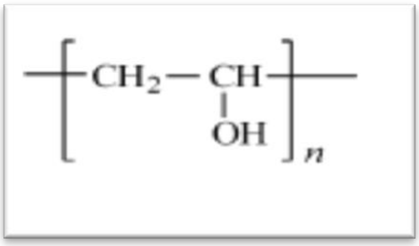

Figure (4): The structure of PVA .

2.4.The solvent (Ethanol)

It is an organic solvent logical name (Ethyl Alcohol) and chemical formula (C_2H_5OH) and atomic weight has (46.07g/ mol) , which solution polar base. The study employments utilizes pure ethanol (99.99%). The properties of this solvent were displayed in table (2) and the ethanol molecule was clarified in figure (5).

Table (2) The principle qualities of Solvent.

Productive company	Avantor (Netherlands)
Chemical formula	C_2H_6O
Scientific name	Ethyl alcohol
Purity	99.99%

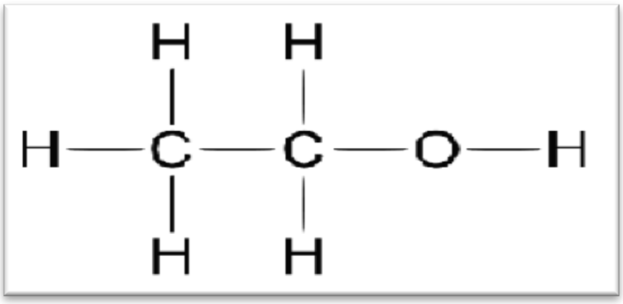

Figure (5): The structure of Ethanol molecule.

2.4. UV-VIS spectrophotometer

UV-VIS spectrophotometer was utilized to measure the absorption spectra for solution and films of fluorescein sodium dye, factory by (Optima, Japan, Aquarius 7000). the properties of this device were displayed in table (3).

Table (3) Specification of the UV-Visible spectrophotometer.

Wavelength range	190nm-1100nm
Wavelength scan rate	Maximum 1000 nm / min
Detector	Silicon photodiode
Power requirements	220-240V.AC
Light source	6V 10 W Tungsten halogen lamp

Figure (6) : UV-Visible Spectrophotometer.

2.5. Spectrofluorometer

Spectrofluorometer (F96 pro) was utilized to measure the fluorescence spectra for films, factory by (chinese-made),the properties of this device were displayed in table (4).

Table (4): Specification of the fluorescence spectrophotometer.

Spectral Range (Ex & Em)	200 to 700 nm
Detector	High sensitivity photo multiplier tube (PMT)
Scanning rate	200, 400 & 600 nm/min
Power requirement	230V ± 10%, 50 Hz, 1Φ, Max.400 VA
Light source	150 watt Xenon arc lamp
Control	Microprocessor, (computer-optional)

Figure (7) : Device fluorescence Spectrophotometer.

2.6. Thickness measurement

Thickness of film was measured by a device of type (REED CM-8822 coating thickness gauge micrometer factory in Canada), with (0.001 mm) measurement accuracy and range of (0-1000 µm).

Figure: (8) Digital meter.

2.7.Sample preparation

Powder was weighed by using of an electric balance. Concentration ($5x10^{-2}$ M) dye doped polymer PVA, a various thicknesses of films were synthesized by casting method in the ratio 3:1[14]

$$W = \frac{M_w \times C \times V}{1000} \ldots\ldots\ldots\ldots\ldots (3)$$

W : weight of the dissolved dye (gm).

Mw : atomic weight of the dye ($\frac{g}{mol}$).

C : Concentration of the dye ($\frac{mol}{l}$).

V : dissolvable of the dye (ml).

3.RESULTS AND DISCUSSION

3.1. Spectral properties of the films of fluorescein Sodium dye and Polyvinyl alcohol.

The Spectra of absorption and fluorescence for films at thicknesses (4,6,8,10,12 µm) as demonstrated in figure (6) and (7) respectively.

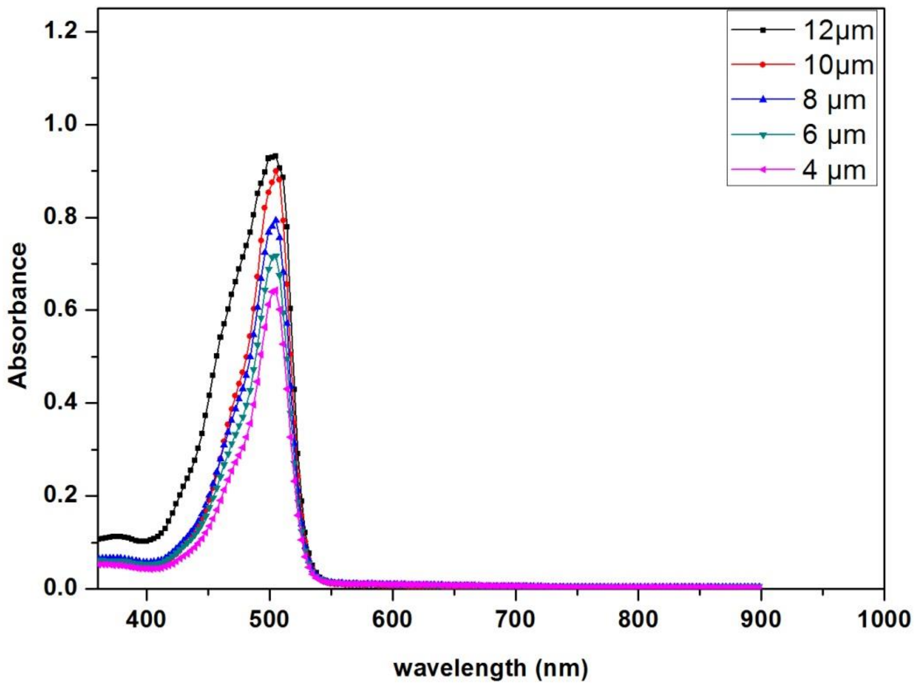

Figure (9): Absorption spectra of thin films at different thickness.

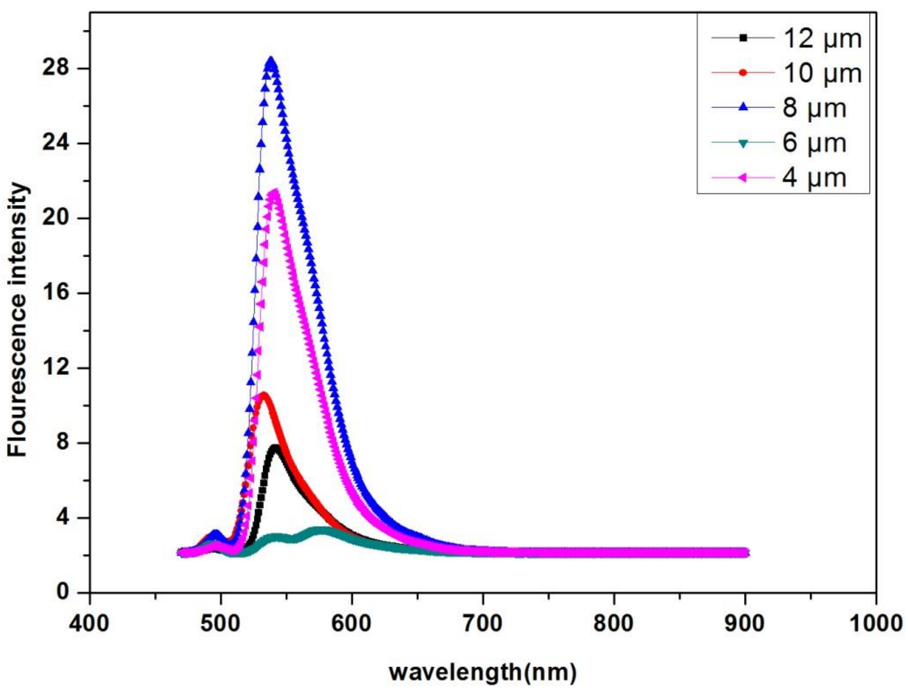

Figure (10): Fluorescence spectra of thin films at different thickness.

The table (5) explains quantum efficiency of various thicknesses.

Table (5): The quantum efficiency.

t(μm)	Φfm%
4	65%
6	66%
8	73%
10	69%
12	78%

The absorption and the fluorescence spectra of the models for various thicknesses (4,6,8,10,12) μm for constant concentration (5×10^{-2}) M pushed towards longer wavelengths (red shift) with increasing thicknesses because of the inecreasing of the number of molecules , however the quantum efficiency increased together.

3.2. Linear 0ptical properties

The linear absorption coefficient of fluorescein Sodium and Polyvinyl alcohol was dictated by utilizing this formulae [15].

$\alpha = \frac{1}{t} \ln \frac{1}{T}$ ... ... (4)

Where

t:sample thickness.

T:transmission.

the extinction coefficient[16].

$K = \frac{\lambda \times \alpha}{4\pi}$ ... ... (5) where, λ : the wavelength of the beam.

The table explains linear optical properties as appeared below.

Table (6): Linear optical properties.

t (μm)	T% (532nm)	α (cm^{-1})	$K\times10^{-7}$	n
4	0.8979	269.24	11404.11	1.6039
6	0.8809	211.35	8952.08	1.6724
8	0.8696	174.65	7397.59	1.7177
10	0.8621	148.38	6284.88	1.7477
12	0.8374	147.87	6263.28	1.8468

3.3. Nonlinear optical properties

The T_p and T_v to compute (n_2) by utilizing this formula [1].

$n_2 = \frac{\Delta\emptyset_0}{I_0 L_{eff} k}$ ... ... (6) where, n_2: nonlinear refractive index.

Where

$\Delta T_{p-v} = 0.406 \Delta\emptyset_0$ ... ... (7)

$\Delta T_{P-V} = T_P - T_V$ ... ... (8)

$K = \frac{2\pi}{\lambda}$ ... ... (9)

$I_0 = \frac{2p}{\pi w_0^2}$ ... ... (10) [17]

Where, T_p : max peak at the close aperture.

T_v :min valley at the close aperture.

ΔT_{P-V} :change in normalized transmittance between peak and valley, which it is equal $|T_p-T_v|$.

$\Delta\emptyset_0$: nonlinear phase shift.

I_0 : intensity of the laser beam at Z = 0.

W_0: the beam waist at the focal point.
P : the power of laser of laser.

$$L_{eff} = \frac{1-\exp^{-\alpha_0 t}}{\alpha_0} \ldots\ldots\ldots\ldots\ldots (11)$$

L_{eff} : effective length of sample.
t : sample thicknesses.
α :linear absorption coefficient.
the ΔT to determine β by utilizing this formula [17].

$$\beta = \frac{2\sqrt{2}}{I_0 L_{eff}} \Delta T \ldots\ldots\ldots\ldots\ldots (12)$$ where β :nonlinear absorption coefficient.

ΔT:is the value of max peak or min valley at the open aperture.

The figures demonstrate (n_2) and(β) respectively at various thicknesses.

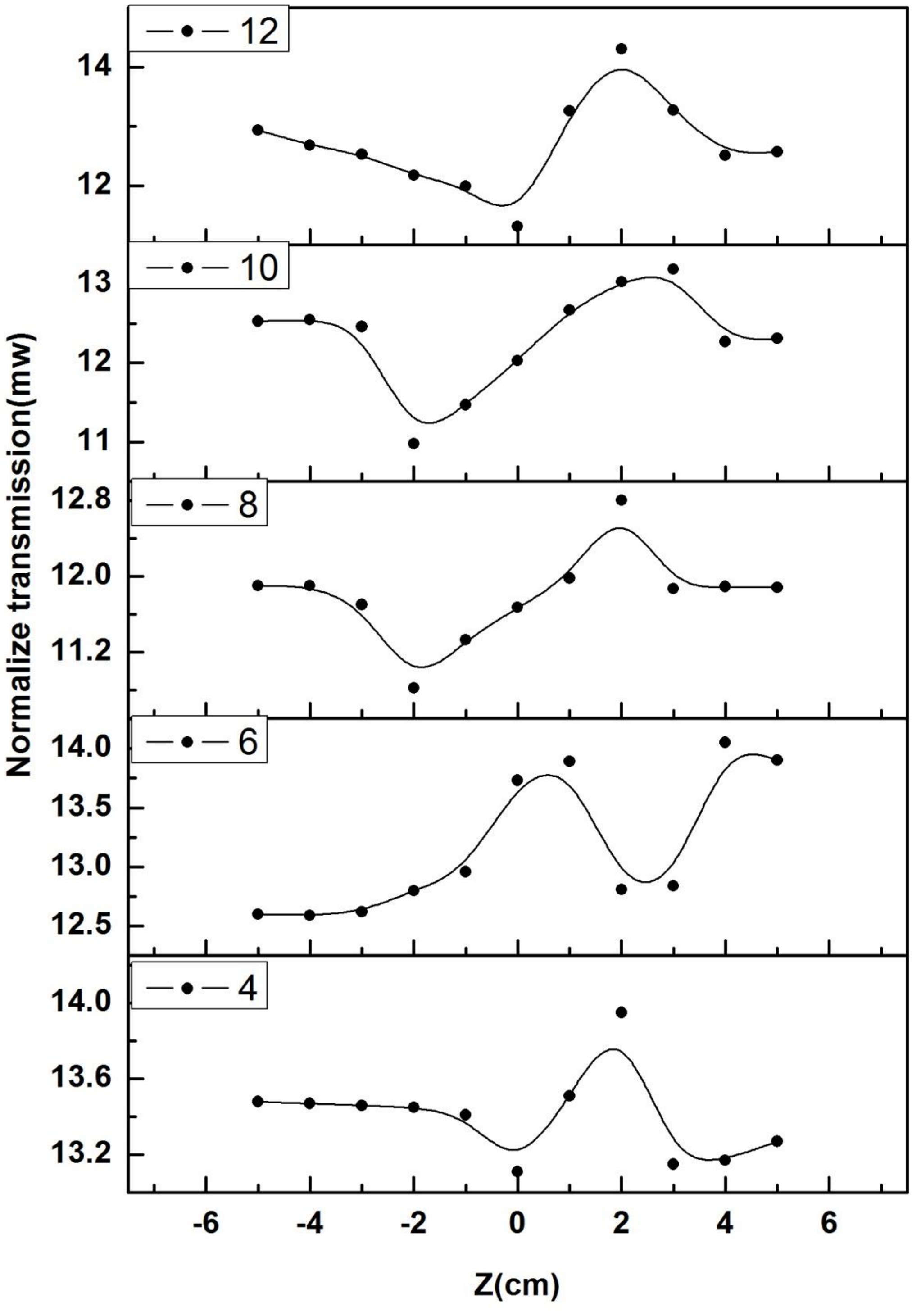

Figure (11): Closed-aperture Z-Scan.

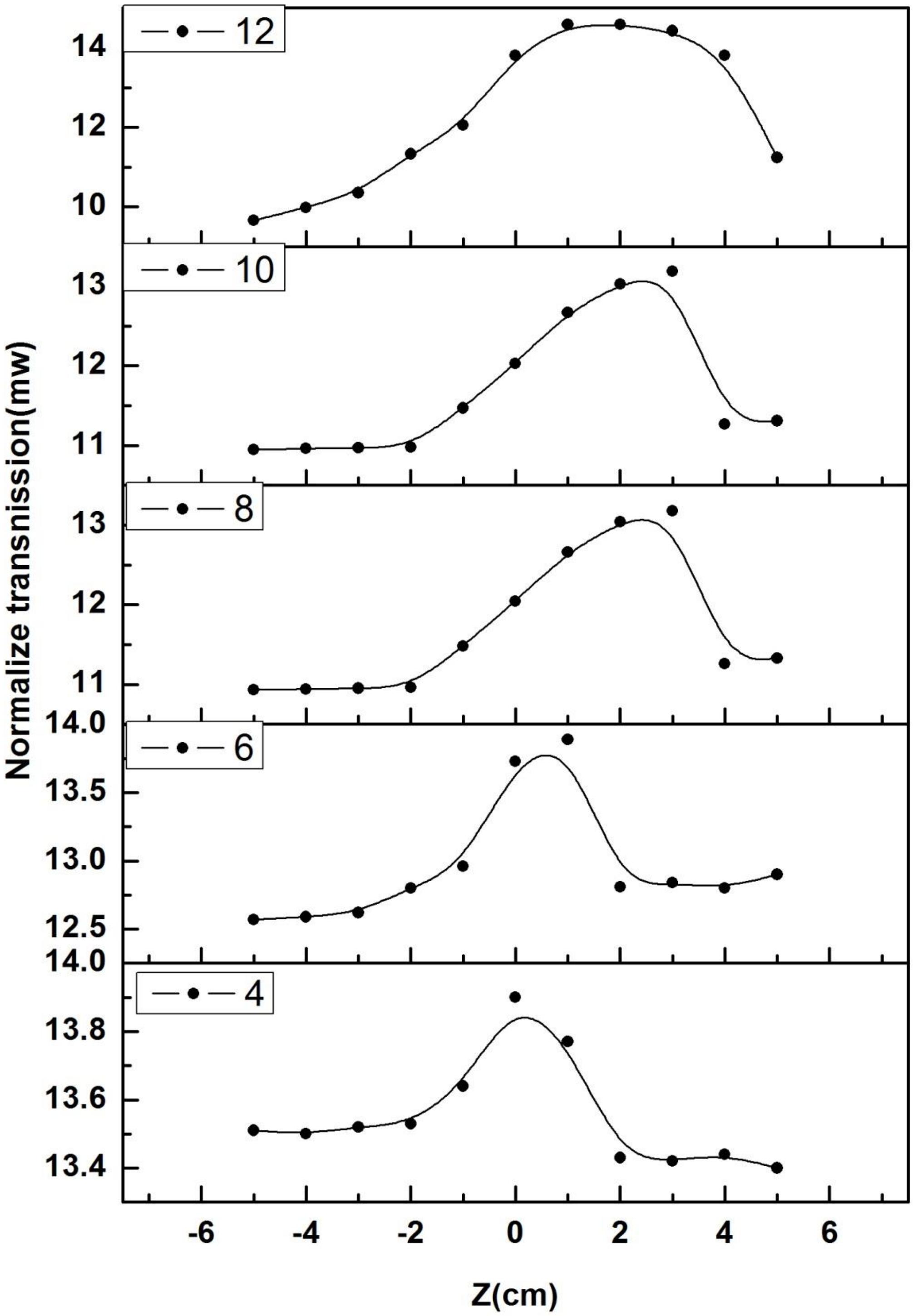

Figure (12): Open -aperture Z-Scan.

The table (7) show the values of(n_2) and (β) as demonstrated below at power 21mW.

Table (7): The nonlinear optical properties.

t (µm)	ΔT_{P-V}	$\Delta\emptyset$ (Rad.)	$n_2(\frac{cm^2}{mw}) \times 10^{-7}$	T_{max}	$\beta\ (\frac{cm}{mw}) \times 10^{-1}$
4	0.84	2.0689	11.2	13.9	25.1
6	1.08	2.6600	9.69	13.89	16.9
8	1.98	4.8768	13.4	13.18	12.1
10	2.21	5.4433	12	13.19	9.72
12	3	7.3891	13.8	14.58	9.08

From this table it can be demonstrated that higher non-linear refractive index (n_2) obtained when the thickness is (12µm), we additionally take note that the non-linear absorption coefficient (β) decreased with increasing thicknesses .The non-linear refractive index changes between positive (self –focusing :in which the order its entirety valley-peak),and negative (self-defocusing: in which the order its entirety peak-valley).The non-linear absorption coefficient displayed the behavior of saturated absorption.

The figures demonstrate (n_2) and(β) respectively at various thicknesses.

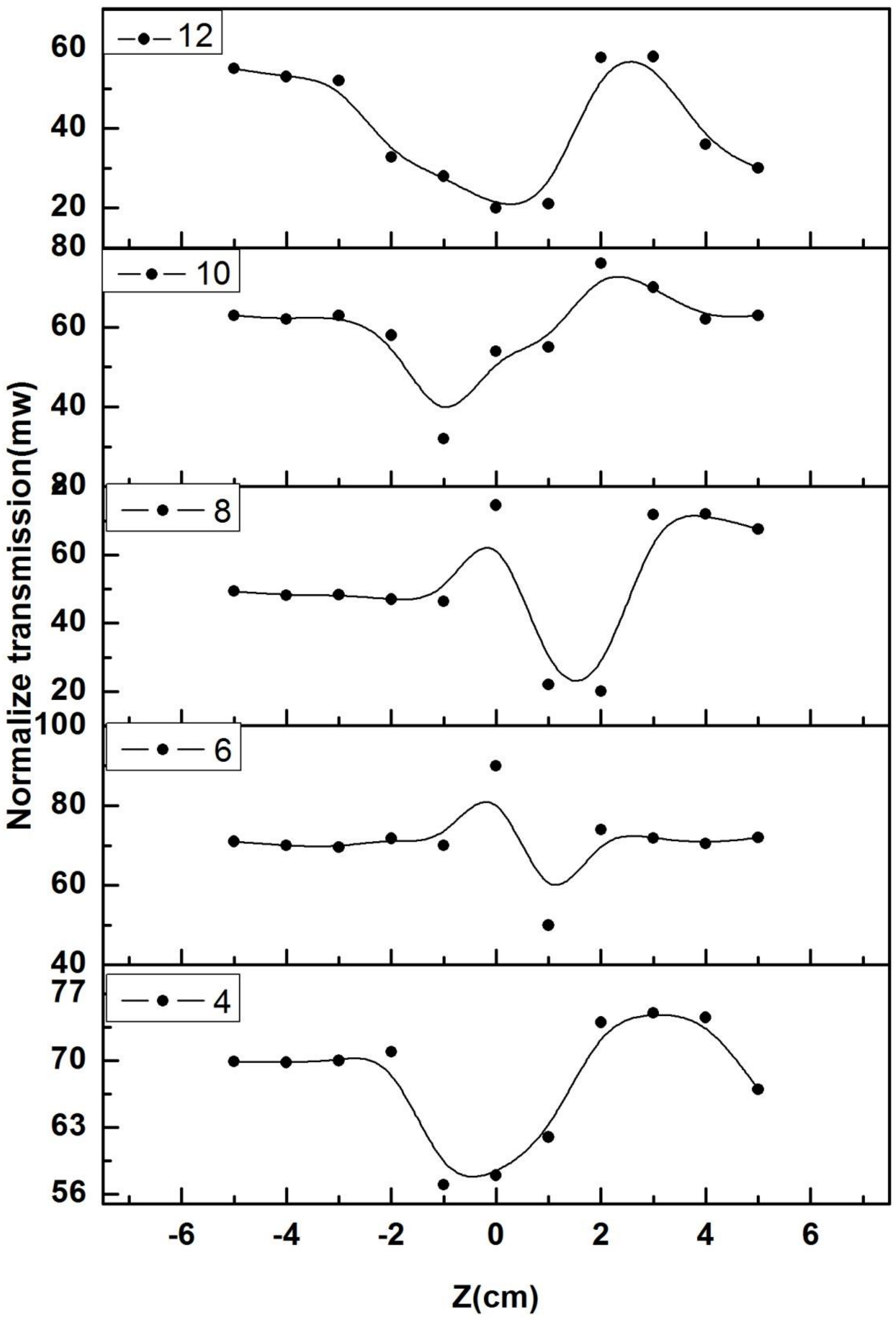

Figure (13): Close -aperture Z-Scan.

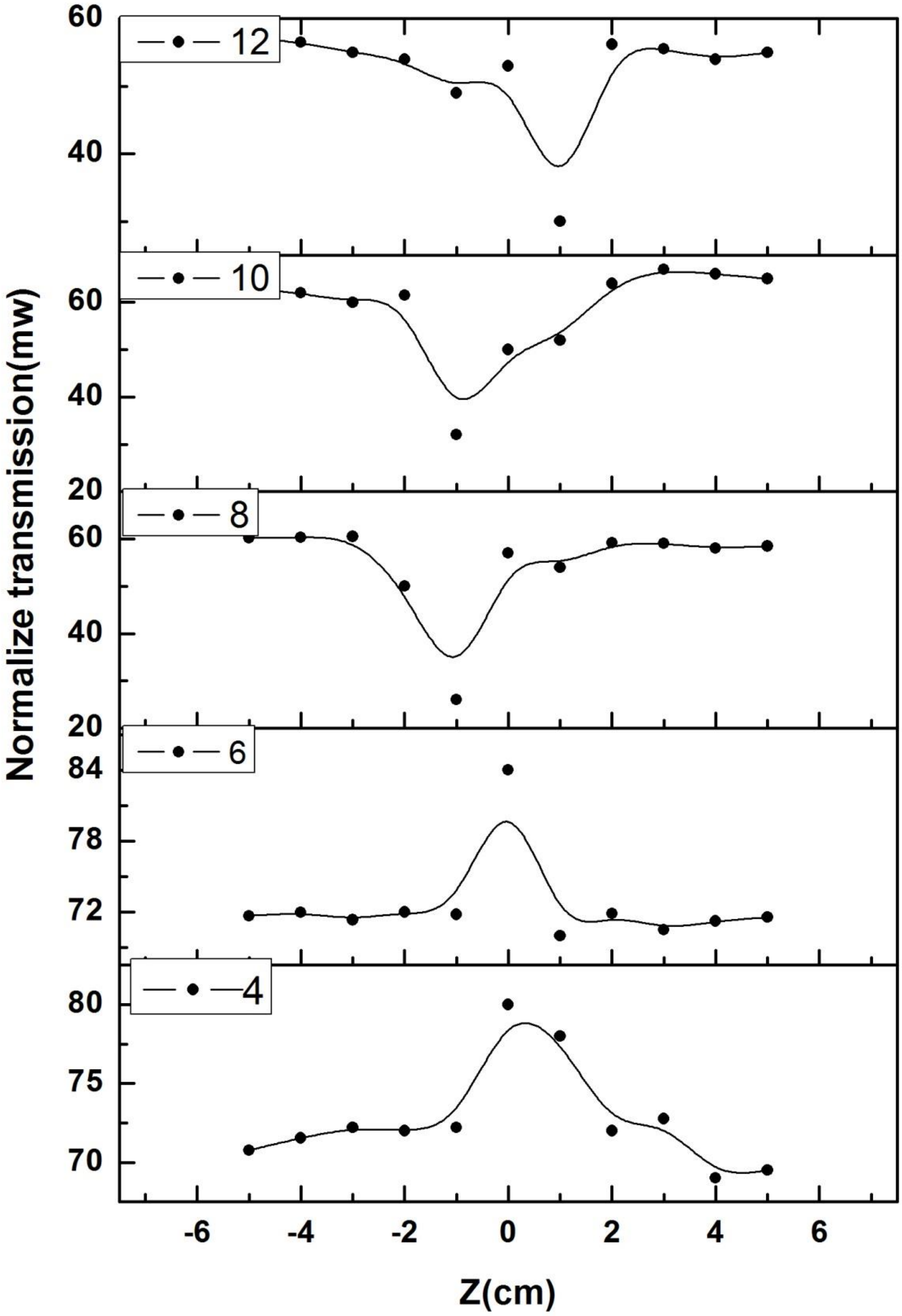

Figure (14): Open -aperture Z-Scan.

The table (8) explains the value of (n_2) and (β) as appeared below at power 80 mW.

Table (8): The nonlinear optical properties.

t (μm)	ΔT_{P-V}	$\Delta\emptyset$ (Rad.)	$n_2 (\frac{cm^2}{mw}) \times 10^{-7}$	T_{max}	$\beta (\frac{cm}{mw}) \times 10^{-1}$
4	18	44.3349	63	80	38
6	40	98.5221	94.2	71.8	22.9
8	54.51	134.2611	96.9	26	6.27
10	44	108.3744	62.8	32	6.20
12	38	93.5960	45.9	30	4.91

From this table it can be demonstrated that higher nonlinear refractive index (n_2) obtained when the thickness is (8 μm), we additionally take note of that higher non-linear absorption coefficient (β) decreased with increasing thicknesses. The non-linear refractive index changes between positive (self –focusing :in which the order its entirety valley-peak),and negative (self-defocusing: in which the order its entirety peak-valley).The non-linear absorption coefficient displayed the behavior of Two-Photon Absorption at (8,10,12) μm and saturated absorption of other concentrations.

The empirical part values was determined ,dye doped film have larger values compared to liquid state [18],therefore the nonlinear optical properties of the solid state are clearer than the liquid [19,20].

4.CONCLUSION

In the present work the conclusions demonstrate the absorption and the fluorescence spectra of the models for various thicknesses shifted towards longer wavelengths. The z-scan measurements demonstrate that the fluorescein sodium dye standard sample display non-linear properties. The nonlinear refractive index and absorption for fluorescein sodium dye with (532nm) (Nd:YAG) CW laser with power (21,80) mW at various thicknesses have been determined.

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