

Optical nonlinearity investigations of the Tetracarbonyl(2,2'-bipyridyl)tungsten(0) using z-scan technique

M. D. ZIDAN^{*a}, M. M. AL-KTAIFANI^b, A. ALLAHHAM^a, H. RIHAWI^a, K. LATIFI^b

^aDepartment of Physics, Atomic Energy Commission, P. O. Box 6091, Damascus, Syria

^bDepartment of Radioisotopes, Atomic Energy Commission, P. O. Box 6091, Damascus, Syria

A CW diode laser ($\lambda = 635$ nm, 26 mW) has been used in the z-scan experiment to evaluate the 3rd nonlinear optical parameters of tetracarbonyl(2,2'-bipyridyl)tungsten(0) in CHCl_3 at two different concentrations. The results indicated that the nonlinear parameters; such as the nonlinear absorption (β) and nonlinear refractive index (n_2) increase with more concentrated solution. Also, the nonlinear parameter (β) values decrease with increase in input intensity (I_0). The new tungsten complex may be considered for future optical applications.

(Received June 12, 2017; accepted June 7, 2018)

Keywords: Tetracarbonyl(2,2'-bipyridyl)tungsten(0), Organometallic complex, Z-scan technique

1. Introduction

Organometallic materials with large nonlinear optical susceptibility (χ^3) have considerable attentions due to their potential applications in various optoelectronic devices, such as human eyes and optical sensors protection from high power laser beams [1-3]. Such important applications have encouraged the scientists to find new organometallic complexes to serve as passive optical modulator for potential optical applications. Recently, there are a number of new optical limiting materials that exhibited nonlinear optical effect. The delocalization of π -electrons and the transfer of electrons between the metal center and the ligands make the organometallic complexes exhibit large third NLO effects.

The popular z-scan technique [4-5] is considered to be effective tools for determining the 3rd nonlinear optical coefficients for different nonlinear optical materials, including organic molecules [6-8], organic dyes [9], fullerenes molecules [10-11], and organometallic complexes [12-23].

To explore the nonlinear optical properties of organometallic complexes, very recently, we have reported the nonlinear optical absorptions of tetracarbonyl (2,2'-bipyridyl)molybdenum(0) [24], 1,1'-Methylenedipyridinium tetrachloridocuprate(II) [25] and tris(2,2'-bipyridyl)iron(II) tetrafluoroborate [26]. In this article, the well-known method "z-scan" was utilized to estimate the nonlinear optical parameters of the tetracarbonyl(2,2'-bipyridyl)tungsten(0) complex. Our objective is to find the figures of merit of the nonlinear parameter of the tungsten(0) complex. This presents a strong indication to use such tungsten(0) complex in the field of nonlinear optical application.

2. Experimental

Tetracarbonyl(2,2'-bipyridyl)tungsten(0) is prepared according to literature method that described in the reference [27]. The hexacarbonyltungsten(0) and 2,2'-bipyridine purchased from (MERCK) and used as received. Fig. 1 depicts the structure of Tetracarbonyl(2,2'-bipyridyl)tungsten(0). The Ultra-Violet-Visible spectrum of the sample was recorded between the 230 and 800 nm using UV-3101 PC Shimadzu Spectrophotometer and is depicted in Fig. 2. The broad absorption bands between 230 and 310 nm can be assigned to the π -bands of the pyridyl subunit. This π -band is also called the conjugation band as its position and intensity was reported to reflect the extent of conjugation in the bipyridyl core [28].

The experimental set-up was described with full details in ref. [6]. The measurements were done with linearly polarized TEM00 Gaussian beam of a CW Diode laser ($\lambda = 635$ nm). The experimental parameters were used as follow: the beam of the CW laser was focused by a 10 cm focal length lens to a waist radius (ω_0) of $34\mu\text{m}$ at the focal point. The diffraction length (Rayleigh length) z_0 is 5.71 mm, the radius of the aperture (r_a) was 0.5 mm and the radius of the beam waist (ω_a) was 1mm on the aperture. The errors in the present measurements (Table 2) arise from the uncertainties in the measuring of the focal spot size ($\pm 5\%$), linear refractive index ($\pm 0.3\%$), linear absorption coefficient ($\pm 5\%$) and Rayleigh length ($\pm 4\%$). The maximum error in such measurements should be less than 5% for each parameter. The studied samples were prepared with two concentrations of 5×10^{-4} M and 1×10^{-4} M. The sample cell was 2 mm thick which fixed on translational stage, and moved across the focal region

along the direction of the propagation of the laser beam. Both the transmitted and reference laser beams were measured with optical detector (ThorlabsPM300E). Consequently, the transmitted signals were acquired, stored, and later on processed by a computer.

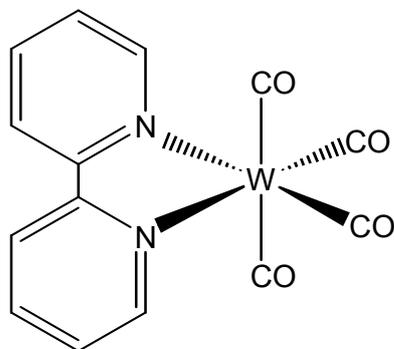


Fig. 1. The structure of tetracarbonyl(2,2'-bipyridyl)tungsten(0)

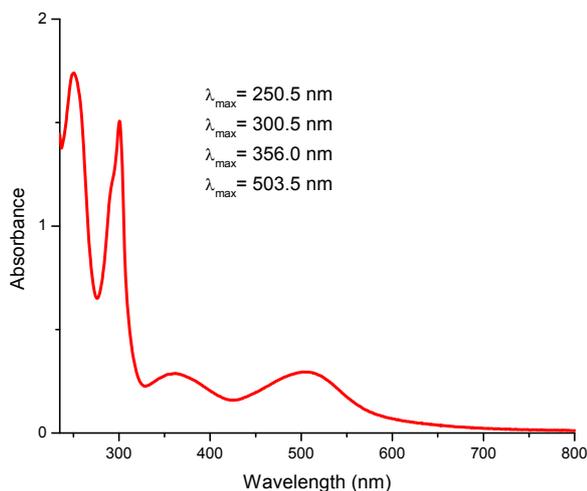


Fig. 2. UV-vis spectrum of tetracarbonyl(2,2'-bipyridyl)tungsten(0)

3. Results and discussion

The obtained UV-Vis spectrum of tetracarbonyl(2,2'-bipyridyl) tungsten(0) is quite informative (Fig. 2), exhibiting four distinctive maximum absorption peaks at 250.5, 300.5, 356 and 503.5 nm. The remarkable shift of absorption peaks for the organometallic complex toward longer wavelengths (visible region) comparing to the parent ligand 2,2'-bipyridyl and $W(CO)_6$ fragment gives strong indication that the energy " ΔE " between the appropriate highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO) of the complex is effectively decreased. As a result of the complex formation $[W(CO)_4(2,2'-bpy)]$, the two rings of W-coordinated bidentate 2,2'-bipyridyl ligand are forced to be relatively coplanar, which enhances the conjugation of the delocalized π -electron system ($\pi \rightarrow \pi^*$ transition is very considerably shifted to lower energy) and also

significantly reduces energy difference for $d \rightarrow d$ transition and metal-ligand charge transfer (MLCT) transitions.

In the present investigation, z-scan technique was employed to extract the two parameters n_2 and β of tetracarbonyl(2,2'-bipyridyl)tungsten(0) in chloroform solution at an input intensity of $I_0 = 826 \text{ W/cm}^2$.

Fig. 3 displays the open aperture z-scan experimental results obtained of the tetracarbonyl(2,2'-bipyridyl)tungsten(0) in $CHCl_3$ at two different concentrations of $5 \times 10^{-4} \text{ M}$ and $1 \times 10^{-4} \text{ M}$. The curves show the characteristic of reverse saturable absorption (RSA), because at higher input intensity " I_0 " the transmittance at focus ($z=0$) will decrease [3-7]. The nonlinear RSA processes in organic compounds with extended π - electrons system have been explained on the bases of the classical five - level model [29-30].

The β coefficient was evaluated from a best fitting performed on the open-aperture (OA) data using Equation 1 [4-5]:

$$T(z) = \sum_{m=0}^{\infty} \frac{(-q_0)^m}{(m+1)^{\frac{3}{2}}} \quad (1)$$

For $q_0 < 1$, Where $q_0(z)$ is a parameter function of I_0 , L_{eff} and β :

$$q_0(z) = \frac{I_0 L_{\text{eff}} \beta}{\left(1 + \frac{z^2}{z_0^2}\right)} \quad (2)$$

Solving the summation and for $\alpha_0 \ll 1$;

$$T(z) = 1 - \frac{(I_0 L_{\text{eff}} \beta)}{\left[2^{\frac{3}{2}} \left(1 + \frac{z^2}{z_0^2}\right)\right]} \quad (3)$$

In the above equations (1-3), $L_{\text{eff}} = (1 - \exp(-\alpha_0 L))/\alpha_0$ is the effective thickness of the sample, L is the thickness of the sample, α_0 is the linear absorption coefficient, $z_0 = \pi \omega_0^2 / \lambda$ is diffraction length of the beam, λ is the laser wavelength, and $I_0 = 826 \text{ W/cm}^2$ is the intensity focus of the beam ($z = 0$). The solid lines (Fig. 3) are the fitting curves while the symbols are the experimental data.

It can be extract from Fig. 4 that the nonlinear absorption coefficient β decreases with increase in the input intensity I_0 , which it means the nonlinearity is the result of TPA and ESA assisted RSA [31]. The ground-state absorption cross section (σ_g) and the excited-state absorption cross section (σ_{ex}) were calculated according to similar method [26]. Their values were listed in Table 2. The resulting values ($\sigma_{\text{ex}} \gg \sigma_g$) confirmed that the nonlinearity here was mostly associated with RSA.

Fig. 5 shows the pure nonlinear refraction curves of the tetracarbonyl(2,2'-bipyridyl)tungsten(0) in $CHCl_3$ at two different concentrations of 5×10^{-4} and $1 \times 10^{-4} \text{ M}$, obtained by division method [8].

To evaluate the nonlinear phase shift at the focus, $\Delta\phi_0$, fitting procedure was applied to the data (the symbols in Fig. 5) using Equation 4 [4-5]:

$$T(z, \Delta\phi) = 1 - \frac{4\Delta\phi_0 X}{(X^2 + 9)(X^2 + 1)} \quad (4)$$

Where is $X = (Z/Z_0)$, and T is the normalized transmittance. After that, the nonlinear refractive index n_2 coefficient can be estimated from equation 5 [4-5]:

$$n_2 = \frac{\lambda \Delta\phi_0}{2\pi I_0 L_{eff}} \quad (5)$$

The real and imaginary parts of the χ^3 are related to the experimental measurements of n_2 and β through the below relations [4-5]:

$$\text{Re } \chi^3 \text{ (esu)} = (10^{-4} \epsilon_0 c^2 n_0^2 / \pi) n_2 \text{ (cm}^2/\text{w)} \quad (6)$$

$$\text{Im } \chi^3 \text{ (esu)} = (10^{-2} \epsilon_0 c^2 n_0^2 \lambda / 4\pi^2) \beta \text{ (cm/w)} \quad (7)$$

Where c and ϵ_0 are the speed of light and vacuum permittivity, respectively.

Both values of α_0 and n_0 were evaluated by described method in ref. [8] and shown in Table 1. All the obtained values of the nonlinear optical parameters such as : n_2 , β , $|\text{Re } \chi^3|$ and $|\text{Im } \chi^3|$ in this work are listed in Table 2.

The peak-valley configuration (Fig. 5) indicates that the tetracarbonyl(2,2'-bipyridyl)tungsten(0) exhibiting self-defocusing effect and negative sign of n_2 . The origin of the self-defocusing effect rose from the absorption of the CW beam, which propagates through an absorbing medium. The variation of the n_2 led to form a thermal lens [32, 33]. The calculated value of n_2 may have contributions of distinct origins, such as electronic (n_2^e) or thermal effects (n_2^{th}), this can be shown by the relation: $n_2 = n_2^e + n_2^{\text{th}}$. The thermal and electronic nonlinearities will have similar effects in z-scan measurements (nonlinear refractive index n_2) but their underlying physical mechanisms are completely different. In the thermal component the sample absorbs incident light, heats up and the index of refraction of the medium is modified due to the increase of temperature. But, in the electronic component the incident light induces nonlinear electronic polarization of the medium and the index of refraction is modified due to the direct interaction of the electromagnetic wave with electrons in the sample. In the electronic component (n_2^e) the effect can be described in terms of the third order optical susceptibility $\text{Re } |\chi^3|$.

Concentration dependence effect was investigated (Figs. 3 and 5). It is indicated that the β and the n_2 parameters are related to the sample concentrations. Both values of β and n_2 increase with more concentrations of the samples. This means that higher concentration; more particles are thermally agitated, resulting enhancement of the thermal nonlinearity [31].

As a CW laser employed in this work, the thermal effect arises from the predominantly non-radiative relaxation of the upper states, which causes a local temperature rise and thus, the thermal n_2 change through the thermo-optic coefficient $\left(\frac{dn}{dT}\right)$ [2, 34].

$$\left(\frac{dn}{dT}\right) = \frac{4 n_2 \kappa}{\alpha_0 w^2 o} \quad (8)$$

where κ is the thermal conductivity of the solvent. Using Equation (8), the thermo-optic coefficient $\left(\frac{dn}{dT}\right)$ of

tetracarbonyl(2,2'-bipyridyl)tungsten(0) with two concentrations of $5 \times 10^{-4} M$ and $1 \times 10^{-4} M$ have been estimated and listed in Table 2.

The experiments were repeated for the pure solvent to find any contribution, but no significantly measurable signals were produced in either the opened/closed data. Also, it was found that the time employed for recording the z-scan data in each plot did not affect the results for evaluating the nonlinear coefficients.

The calculated values of n_2 and β in this work (Table 2) can be compared with other values of n_2 and β of different materials reported [19, 35-39]. It can be seen that tetracarbonyl(2,2'-bipyridyl)tungsten(0) shows large 3rd nonlinear optical properties because of the delocalized electronic states formed by the overlapping between $\pi \rightarrow \pi^*$ and d orbitals [19,40].

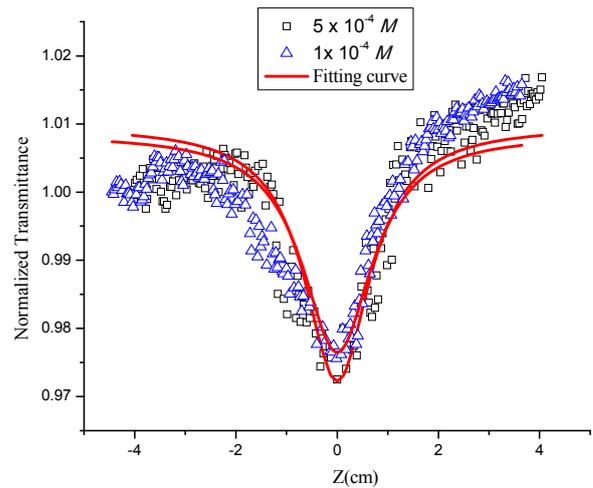


Fig. 3. Open-aperture z-scan data of $5 \times 10^{-4} M$ and $1 \times 10^{-4} M$ of tetracarbonyl(2,2'-bipyridyl)tungsten(0) in CHCl_3 . Solid lines depict the fitting curves

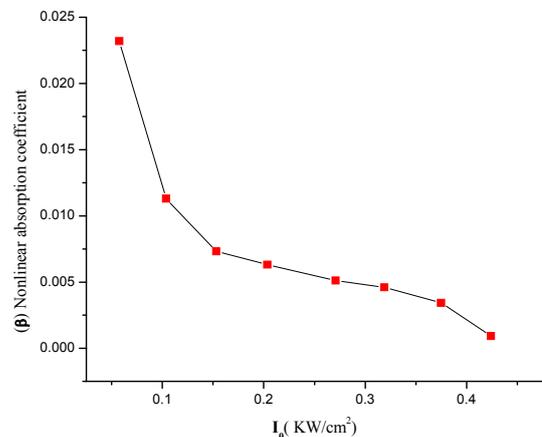


Fig. 4. Nonlinear absorption coefficient β versus the input intensity I_0 of tetracarbonyl(2,2'-bipyridyl)tungsten(0) in CHCl_3

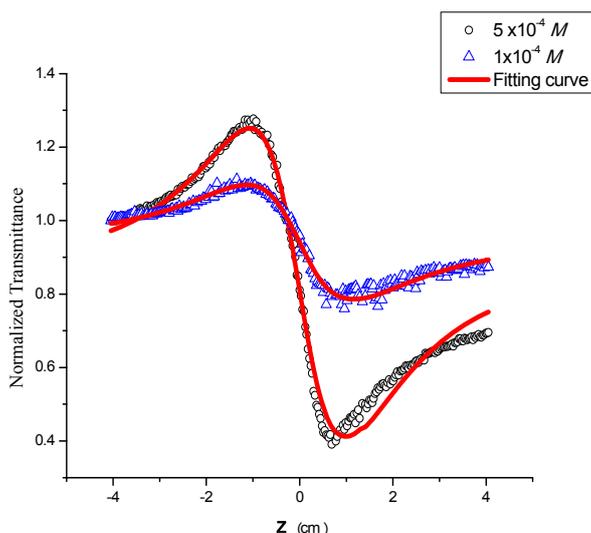


Fig. 5. Pure nonlinear refraction data of $5 \times 10^{-4} M$ and $1 \times 10^{-4} M$ of tetracarbonyl(2,2'-bipyridyl)tungsten(0) in CHCl_3 . Solid lines depict the fitting curves

Table 1. The measured values of linear refractive index n_0 and linear absorption coefficient α_0 of $5 \times 10^{-4} M$ and $1 \times 10^{-4} M$ concentrations of tetracarbonyl(2,2'-bipyridyl)tungsten(0)

Concentration (m/l)	α_0 (cm^{-1})	n_0
5×10^{-4}	0.77	1.449
1×10^{-4}	0.47	1.448

Table 2. The calculated nonlinear parameters of $5 \times 10^{-4} M$ and $1 \times 10^{-4} M$ concentrations of tetracarbonyl(2,2'-bipyridyl)tungsten(0) solutions

Concentration (m/l)	β (cm/W)	n_2 (cm^2/W)	σ_g (cm^2)	σ_{ex} (cm^2)	$\frac{dn}{dT}$ (K^{-1})	$\text{Re}(\chi^3)$ (esu)	$\text{Im}(\chi^3)$ (esu)
5×10^{-4}	6.89×10^{-4}	1.36×10^{-7}	2.56×10^{-18}	5.53×10^{-14}	1.74×10^{-4}	7.24×10^{-6}	1.85×10^{-5}
1×10^{-4}	6.11×10^{-4}	0.49×10^{-7}	1.56×10^{-18}	8.04×10^{-14}	1.03×10^{-4}	2.63×10^{-6}	1.64×10^{-5}

4. Conclusion

In summary, we have demonstrated the z-scan experiment of the organometallic complex tetracarbonyl(2,2'-bipyridyl)tungsten(0), using a CW diode Laser at 635 nm wavelength. According to the experimental results, the values of α_0 , n_0 , n_2 , β , $\text{Re}|\chi^3|$, and $\text{Im}|\chi^3|$ are estimated, and they are affected by the nature of attached ligand. As expected, in the organometallic complex tetracarbonyl(2,2'-bipyridyl)tungsten(0), the combination of the organic fragment 2,2'-bipyridyl (with delocalized π -electrons system) and the inorganic part $\text{W}(\text{CO})_4$ (with d orbitals and π -electrons system) led to a relatively characteristic optical nonlinearity property.

Acknowledgements

We appreciate help of Prof. I. Othman, Prof. A. H. Al-Rayyes and Prof. M. K. Sabra.

References

- [1] B. J. Coe, M. Samoc, A. Samoc, L. Zhu, Y. Yi, Z. Shuai, *J. Phys. Chem. A* **111**(3), 472 (2007).
- [2] H. L. Saadon, Basil Ali, Adil A. Al-Fregi, *Opt. Laser Technol.* **58**, 33 (2014).
- [3] B. Sahraoui, M. Sylla, J. P. Bourdin, G. Rivoire, J. Zarembaj, *J. of Modern Optics* **42**(10), 2095 (1995).
- [4] M. Sheik-Bahae, A. A. Said, E. W. Van Stryland, *Opt. Lett.* **14**, 955 (1989).

- [5] M. Sheik-Bahae, A. A. Said, T. Wei, D. J. Hagan, E. W. Van Stryland, *IEEE J. Quantum Electron.* **QE-26**, 760 (1990).
- [6] B. Chandrakantha, A. M. Isloor, R. Philip, M. Mohesh, P. Shetty, A.M. Vijesh, *Bull. Mater. Science* **34**, 887 (2011).
- [7] A. W. Allaf, M. D. Zidan, *Laser Physics* **14**, 1529 (2004).
- [8] M. D. Zidan, M. Al-Ktaifani, A. Allahham, *Opt. Laser Technol.* **70**, 45 (2015).
- [9] S. Pramodini, P. Poornesh, *Opt. Laser Technol.* **63**, 114 (2014).
- [10] H. I. Elim, J. Ouyang, J. He, S. H. Goh, S. H. Tang, W. Ji, *Chem. Phys. Lett.* **369**, 281 (2003).
- [11] A. R. Kost, J. E. Jensen, R. O. Loufty, J. C. Wither, *Applied Physics B* **80**, 281 (2005).
- [12] Yun-Dong Zhang, Zhen-YuZhao, Cheng-BaoYao, LanYang, JinLi, PingYuan, *Opt. Laser Technol.* **58**, 207 (2014).
- [13] H. Fan, X. Wang, Q. Ren, X. Zhao, G. Zhang, J. Chen, D. Xu, G. Yu, Z. Sun, *Opt. Laser Technol.* **42**, 732 (2010).
- [14] C. Yao, Y. Zhang, H. Yin, Q. Meng, C. Yu, J. Li, P. Yuan, *Chem. Phys. Lett.* **576**, 35 (2013).
- [15] Y. Ji, J. Zuo, L. Chen, Y. Tian, Y. Song, Y. Li, X. You, *J. Phys. Chem. Solids* **66**, 207 (2005).
- [16] Y. Cheng, Y. Mao, J. Liu, S. Feng, T. He, *Journal of Modern Optics* **54**, 2763 (2007).
- [17] K. B. Manjunatha, R. Dileep, G. Umesh, B. Ramachandra, *Materials Letters* **105**, 173 (2013).
- [18] T. C. Sabari Girisun, S. Dhanuskodi, G. Vinitha, *Materials Chemistry and Physics* **129**, 9 (2011).
- [19] H. Fan, Q. Ren, X. Wang, T. Li, J. Sun, G. Zhang, D. Xu, G. Yu, Z. Sun, *Natural Science* **1**, 136 (2009).
- [20] Q. Ren, X. B. Sun, X. Q. Wang, G. H. Zhang, X. D. Yang, F. J. Zhang, H. I. Yang, Y. T. Chow, D. Xu, *Appl. Phys. A.* **90**, 685 (2008).
- [21] J. Sun, W. F. Guo, X. Q. Wang, G. H. Zhang, X. B. Sun, L.Y. Zhu, Q. Ren, D. Xu, *Opt. Commun.* **280**, 183 (2007).
- [22] I. Guezguez, A. Ayadi, K. Ordon, K. Iliopoulos, Diana G. Branzea, A. Migalska-Zalas, M. Makowska-Janusik, A. El-Ghayoury, B. Sahraoui, *J. Phys. Chem. C* **118**, 7545 (2014).
- [23] H. Li, Z. Chen, L. Cheng, J. Liu, X. Chen, J. Li, *Cryst. Growth Des.* **8**, 4355 (2008).
- [24] M. D. Zidan, M. M. Al-Ktaifani, A. Allahham, *Optik* **127**, 2570 (2016).
- [25] M. D. Zidan, M. M. Al-Ktaifani, A. Allahham, *Optik* **127**, 4443 (2016).
- [26] M. D. Zidan, M. M. Al-Ktaifani, A. Allahham, *Opt. Laser Technol.* **90**, 174 (2017).
- [27] M. H. B. Stiddard, *J. Chem. Soc.* **0**, 4712 (1962). DOI: 10.1039/JR9620004712
- [28] M. Gantenbein, Terminally diisocyano functionalized and rotationally restricted biphenyl systems, M.Sc. Thesis, Switzerland, University of Basel, 2010.
- [29] P. Lind, Organic and Organometallic Compounds for Nonlinear Absorption of Light, M.Sc. Thesis, Sweden, Umeå University, 2007.
- [30] N. K. Siji Narendran, R. Soman, C. Arunkumar, K. Chandrasekharan, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **136**, 838 (2015).
- [31] S. Pramodini, P. Poornesh, *Opt. Laser Technol.* **62**, 12 (2014).
- [32] M. D. Zidan, A. W. Allaf, M. B. Alsous, A. Allahham, *Opt. Laser Technol.* **58**, 128 (2014).
- [33] S. Zafar, Z. H. Khan, M. S. Khan, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **114**, 164 (2013).
- [34] F. Z. Henari, W. J. Blau, *Proc. SPIE* **2854**, 174 (1996).
- [35] S. Pramodini, P. Poornesh, Y. N. Sudhakar, M. Selva Kumar, *Opt. Commun.* **293**, 125 (2013).
- [36] T. Ceyhan, G. Yağlıoğlu, H. Unver, B. Salih, M. K. Erbil, A. Elmali, O. Bekaroğlu, *Macroheterocycles* **1(1)**, 44 (2008).
- [37] S. Dhanuskodi, T. C. Sabari Girisun, S. Vinitha, *Current Applied Physics* **11**, 860 (2011).
- [38] M. D. Zidan, M. Alktaifani, A. Allahham, *Optik* **126**, 1491 (2015).
- [39] B. Derkowska, M. Wojdyła, R. Czaplicki, W. Bała, B. Sahraoui, *Opt. Commun.* **274**, 206 (2007).
- [40] I. Papagiannouli, K. Iliopoulos, D. Gindre, B. Sahraoui, O. Krupka, V. Smokal, A. Kolendo, S. Couris, *Chem. Phys. Lett.* **554**, 107 (2012).

*Corresponding author: PScientific8@aec.org.sy