

Z-scan measurement of optical nonlinearity of the tetracarbonyl(2,2'-bipyridyl)chromium(0) complex

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The optical nonlinearity of the tetracarbonyl(2,2'-bipyridyl)chromium(0) in chloroform solution was investigated utilizing z-scan technique. The basic parameters were estimated from the fitting of the experimental data, including the nonlinear coefficient (β), the nonlinear refractive index (n_2), the cross section of absorption ground-state (σ_g), the cross section of absorption excited-state (σ_{ex}) and thermo-optic coefficient. The resulting values $\sigma_{ex} \gg \sigma_g$ have confirmed that the studied compound has the property of reverse saturable absorption (RSA) mechanism. Our results show that the value of β is negative; it decreases with increasing the input power irradiance (I_0) and the variation of nonlinear refractive index (n_2) due to thermal effect. The tetracarbonyl (2,2'-bipyridyl)chromium(0) might have a potential application in the optical limiting field.

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1. Introduction

Organometallic materials with large third-order nonlinear optical susceptibility have considerable attentions due to their potential applications in various optoelectronic devices [1- 4]. As a result of their ease in chemical alteration and reduction in cost, these materials may replace the typical inorganic NLO crystals [5]. In organometallic complexes, the d electrons of the transition metal center have usually the appropriate energy and symmetry to be involved in delocalization with π -electron system of the organic ligand. In such metal-ligand (ML) system, the electrons are free to move, the nonlinearity is raised from the interaction between light and the free electrons within the ML system [5].

The single beam z-scan technique [6-7] is considered to be an accurate experimental method to determine both nonlinear absorption (β) and refractive index (n_2). The previous works have concentrated on the synthesis and characterization properties of organometallic compounds. But, limited number of articles was reported on the nonlinearity of ML system using z-scan technique [8-14].

As we are currently interested to explore the 3rd nonlinear optical (NLO) properties of organometallic complexes, and we have recently reported the NLO properties of the tetracarbonyl(2,2'-bipyridyl)molybdenum(0) [15], 1,1'-Methylenedipyridinium tetrachloridocuprate(II) [16] and tris(2,2'-bipyridyl)iron(II) tetrafluoroborate [17]. In this article, we present the 3rd nonlinear optical (NLO) properties of the organometallic complex "tetracarbonyl(2,2'-bipyridyl)chromium(0) in chloroform (CHCl₃) solution" using z-scan technique at 635 nm wavelength. To the best of our knowledge, no reports are available in literature, regarding the NLO properties of the

studied complex. We can claim the novelty of our work is study of the new prepared tetracarbonyl(2,2'-bipyridyl)chromium(0) complex using z-scan technique. Although, it is considered as an old technique, but it has been used as simple method to determine the nonlinear optical parameters of new molecules. This leads to find the figures of merit of the nonlinear parameter of the chromium complex. This kind of study gives a strong indication to use such chromium complex in the field of nonlinear optical application.

2. Experimental techniques

The tetracarbonyl(2,2'-bipyridyl)chromium(0) was prepared according to the reported method in ref. [18] as follow: A mixture of hexacarbonylchromium(0) (0.55 g, 2.50 mmol) and (2,2'-bipyridyl) (0.40 g, 2.56 mmol) was refluxed in toluene (25 ml) under N₂ atmosphere for 2 hours. A powdery precipitate was obtained on cooling, which was filtered off and washed with hexane (3×5ml) and dried in vacuo to give tetracarbonyl(2,2'-bipyridyl)chromium(0) as a dark orange powder (0.4 g, 50 %). Fig. 1 depicts the molecular structure of tetracarbonyl(2,2'-bipyridyl)chromium(0). The Ultra-violet-visible (UV-Vis) spectrum of the sample in the range of 230- 700 nm was acquired by the UV-3101 PC Shimadzu Spectrophotometer. The absorption spectrum of tetracarbonyl(2,2'-bipyridyl)chromium(0) shows three characteristic peaks centred at 240, 305 and 410 nm (Fig. 2). The notable longer wave length shifting of absorption bands of the complex comparing to 2,2'-bipyridyl and Cr(CO)₆ is readily attributed to the pronounced decrease of energy difference between the related HOMO and LUMO states of the complex. The formation of the complex

makes the two rings of the 2,2'-bipyridyl more coplanar, which augments the aromatic conjugation of the bidentate 2,2'-bipyridyl ligand in the complex and enhances significantly the delocalization of π -electrons of the complex. The same observation was reported for the analogous complex tetracarbonyl(2,2'-bipyridyl)molybdenum(0) [19,15].

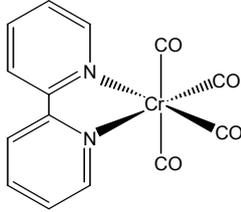


Fig. 1. The structure of tetracarbonyl(2,2'-bipyridyl)chromium(0).

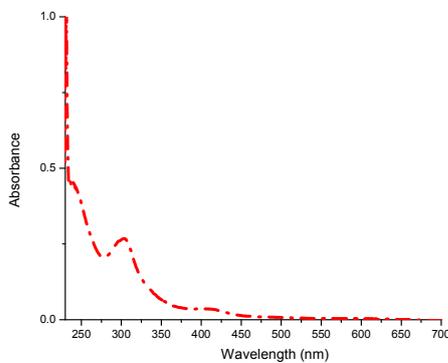


Fig. 2. UV-vis spectrum of tetracarbonyl(2,2'-bipyridyl)chromium(0).

The experimental setup is similar to our previous work [20]. The excitation source was a linearly polarized TEM₀₀ Gaussian beam of diode laser. The laser model is CUBE™ Diode Laser System, Coherent- 635-3QE, it works only in CW regime at $\lambda = 635\text{nm}$ up to 16.4 mW. All the parameters used in the present experiment were mentioned in our previous work [15]. Fig. 3 shows the schematic of the z-scan technique. The sample cell was 2 mm thick quartz which was fixed on a computer-controlled translation stage is precisely moved through the focal area of the beam over a length of 6 cm. A power meter (Thorlabs PM300E) was used to measure the reference beam and transmitted beam powers. All the experimental units were control by a computer for further data processing.

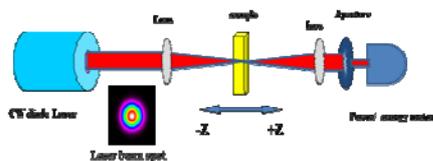


Fig. 3. The schematic of the z-scan technique.

3. Results and discussion

To evaluate the nonlinear coefficients of tetracarbonyl(2,2'-bipyridyl)chromium(0) in chloroform solution, z-scan experiments in open aperture (OA) and closed aperture (CA) configurations were carried out for input intensity of $I_0 = 903 \text{ W/cm}^2$.

Fig. 4 shows the OA results of the tetracarbonyl(2,2'-bipyridyl)chromium(0) in CHCl_3 at a concentration of 10^{-3} M at different input irradiance (I_0). The shape of the curve in Fig. 4 showing a decrease in the value of transmittance around the $z=0$ with an increase of input intensity is the characteristic signature of reverse saturable absorption (RSA) or positive nonlinear absorption. By studying the UV-Vis spectrum of tetracarbonyl(2,2'-bipyridyl) chromium(0), it seems there is no linear absorption nearby the spectral range 635 nm. This suggests the possibility of occurrence of two photon absorption process in our sample. The RSA process was explained on the basis of classical five - level model of organic molecules with extended π - electron systems [15, 21].

The β coefficient obtained from the fitting curve (Solid line) of the experimental data (The symbols) of OA data of normalized transmittance by the equations 1-3 [6-7]:

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

For $q_0 < 1$, Where term $q_0(z)$ is 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 , α_0 , $z_0 = \pi \sqrt{\lambda} / \lambda$ and $I_0 = 903 \text{ W/cm}^2$ are the thickness of the sample, the linear absorption coefficient, diffraction length and the intensity of the beam at focus $z = 0$.

It well-known in the nonlinear regime, the absorption will be a nonlinear function of the excitation intensity I_0 at the focus point, $z = 0$. If the nonlinear absorption coefficient (β) is positive, it increases with increasing the input power (I_0), but if the value of β is negative, it decreases with increasing the input power irradiance (I_0) [22]. Our result in figure 5 shows the relation between the excitation intensity I_0 and the nonlinear absorption coefficient β . The β decreases with increasing of the I_0 , which means that the nonlinearity behavior resulting of two photons absorption

(TPA) and excited state absorption (ESA) assisted RSA process according to the literature [23, 24]. The σ_g and the σ_{ex} were calculated according to similar method [20]. Their values were found to be $\sigma_g = 2.76 \times 10^{-18} \text{ cm}^2$ and $\sigma_{ex} = 3.95 \times 10^{-13} \text{ cm}^2$. The resulting values, $\sigma_{ex} \gg \sigma_g$ confirmed that the nonlinearity here was mostly associated with RSA.

To obtain the n_2 of the tetracarbonyl(2,2'-bipyridyl)chromium(0) in CHCl_3 at a concentration of 10^{-3} M , the on-axis nonlinear phase shift $\Delta\phi_0$ at the focus point was determined through fitting the pure *nonlinear refraction curves* (Fig. 6) with the following equation [6-7]:

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

where $X = (Z/Z_0)$, and T is the normalized transmittance in the fitting curves (The solid line). Then, the coefficient, n_2 , was deduced using the equation 5, [6-7]:

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

From knowledge of the two coefficients n_2 and β , one can compute the corresponding of the third-order nonlinear optical susceptibility, χ^3 , by the following relations [6-7]:

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

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

where ϵ_0 is the vacuum permittivity and c is the speed of light in vacuum.

The values of α_0 and the n_0 obtained in similar method [20]. All the obtained values of α_0 , n_0 , n_2 , β , $|\text{Re} \chi^3|$ and $|\text{Im} \chi^3|$ in this work are listed in Table 1.

Fig. 6 shows that the tetracarbonyl(2,2'-bipyridyl)chromium(0) exhibiting a peak - valley configuration. This suggests that the sign of n_2 negative, also, the sample can be considered as self-defocusing material around 635 nm. The calculated value of n_2 may have contributions of distinct origins, such as electronic (n_2^e) or thermal effects (n_2^{th}). Hence, one can separate such contributions 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 $\text{Re} |\chi^3|$. However, the defocusing effect is raised from the absorption of

the CW laser beam through an absorbing medium. This led to variation of the refractive index, which acts as a thermal lens [25- 27].

The thermal nonlinearity (n_2) is related with the thermo-optic coefficient $\left(\frac{dn}{dT}\right)$ by the equation 8 [28]:

$$\left(\frac{dn}{dT}\right) = \frac{4 n_2 \kappa}{\alpha_0 \omega_0^2} \quad (8)$$

where κ is the thermal conductivity of the solvent ($\kappa = 0.129 \text{ W/m K}$). Using Equation 8, the value of the thermo-optic coefficient $\left(\frac{dn}{dT}\right)$ of tetracarbonyl(2,2'-bipyridyl)chromium(0) in CHCl_3 has been found to be $9.11 \times 10^{-5} (\text{K}^{-1})$.

The same experimental conditions were repeated with the solvent to trace any signal, but nothing was found. Our reported values of n_2 and β of the tetracarbonyl(2,2'-bipyridyl)chromium(0) compound in Table 1 can be compared with the recently reported values in literature for similar molecules with CW laser excitation [13, 29-31]. The 3rd optical nonlinearity in the tetracarbonyl(2,2'-bipyridyl)chromium(0) complex due to the electronic states formed by $\pi \rightarrow \pi^*$ and $d \rightarrow d^*$ transitions, and it is consider to be very promising candidate [15, 32-33].

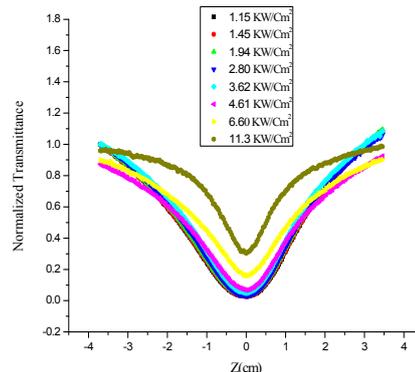


Fig. 4. Open-aperture z-scan data of 10^{-3} M of tetracarbonyl(2,2'-bipyridyl)chromium(0) in chloroform at different input powers.

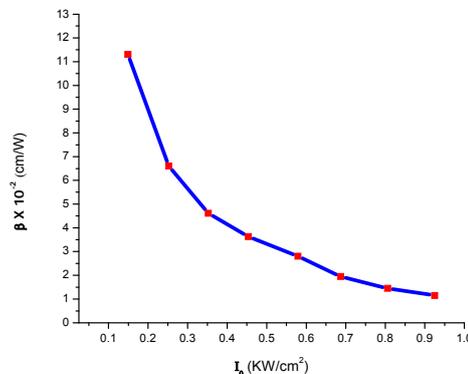


Fig. 5. Nonlinear absorption coefficient β versus on-axis input intensity I_0 of tetracarbonyl(2,2'-bipyridyl)chromium(0) in chloroform.

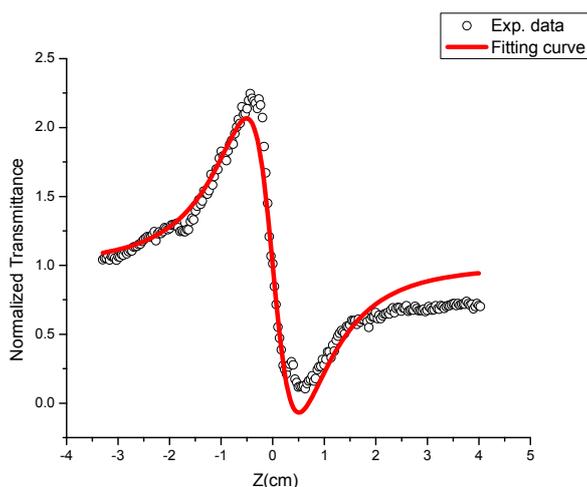


Fig. 6. Pure nonlinear refraction curve of 10^{-3} M of tetracarbonyl(2,2'-bipyridyl)chromium(0) in chloroform.

Table 1. The linear and nonlinear optical parameters of tetracarbonyl(2,2'-bipyridyl)chromium(0) at concentration of 10^{-3} M.

α_0 (cm ⁻¹)	n_0	$n_2 \times 10^{-7}$ (cm ² /W)	$\beta \times 10^{-2}$ (cm/W)	Re(χ^3) $\times 10^{-5}$ (esu)	Im(χ^3) $\times 10^{-4}$ (esu)
1.66	1.441	-3.39	1.06	1.78	2.82

4. Conclusions

In summary, the organometallic complex “tetracarbonyl(2,2'-bipyridyl)chromium(0)” was studied by z-scan method using a diode Laser ($\lambda=635$ nm). The values of α_0 , n_0 , n_2 , β , Re $|\chi^3|$, $|\text{Im}\chi^3|$ and the thermo-optic coefficient were determined. As expected, the combination of the organic fragment 2,2'-bipyridyl and the inorganic part $\text{Cr}(\text{CO})_4$ led to increase the nonlinearity in the chromium complex. The values of β are recorded at different input powers (I_0), it was found that the values of β decrease with increasing the values of I_0 and the changes in the nonlinear refractive index (n_2) due to thermal effect. As seen in the CA data, the sample exhibited a peak-valley configuration, this mean that the sign of the n_2 is negative and this complex should be considered as self-defocusing material around $\lambda=635$ nm.

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References

- [1] S. Tekin, U. Kürüm, M. Durmus, H. G. Yaglioglu, T. Nyokong, A. Elmali, Opt. Comm. **283**, 4749 (2010).
- [2] Y-D Zhang, Z-Y Zhao, C-B Yao, L. Yang, J. Li, P. Yuan, Opt. Laser Technol. **58**, 207 (2014).
- [3] H. Fan, X. Wang, Q. Ren, X. Zhao, G. Zhang, J. Chen, D. Xu, G. Yu, Z. Sun, Opt. Laser Technol. **42**, 732 (2010).
- [4] C. Yao, Y. Zhang, H. Yin, Q. Meng, C. Yu, J. Li, P. Yuan, Chem. Phys. Lett. **576**, 35 (2013).
- [5] T. Huang, Z. Hao, H. Gong, Z. Liu, S. Xiao, S. Li, Y. Zhai, S. You, Q. Wang, J. Qin, Chem. Phys. Lett. **451**, 213 (2008).
- [6] M. Sheik-Bahae, A. A. Said, E. W. Van Stryland, Opt. Lett. **14**, 955 (1989).
- [7] M. Sheik-Bahae, A. A. Said, T. Wei, D. J. Hagan, E. W. Van Stryland, IEEE J. Quantum Electron **QE-26**, 760 (1990).
- [8] K. B. Manjunatha, R. Dileep, G. Umesh, B. Ramachandra **105**, 173 (2013).
- [9] T. C. Sabari Girisun, S. Dhanuskodi, G. Vinitha, Mat. Chem. Phys. **129**, 9 (2011).
- [10] H. Fan, Q. Ren, X. Wang, T. Li, J. Sun, G. Zhang, D. Xu, G. Yu, Z. Sun, Natural Science **1**, 136 (2009).
- [11] 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).
- [12] J. Sun, W. F. Guo, X. Q. Wang, G. H. Zhang, X. B. Sun, L. Y. Zhu, Q. Ren, D. Xu, Opt. Comm. **280**, 183 (2007).
- [13] M. D. Zidan, M. Alktaifani, A. Allahham, Optik **126**,

- 1491 (2015).
- [14] H. Chen, Z. Li, L. Cheng, J. Liu, X. Chen, J. Li, *Cryst. Growth Des.* **8**, 4355 (2008).
- [15] M. D. Zidan, M. M. Al-Ktaifani, A. Allahham, *Optik* **127**, 2570 (2016).
- [16] M. D. Zidan, M. Alktaifani, A. Allahham, *Optik* **127**, 4443 (2016).
- [17] M. D. Zidan, M. M. Al-Ktaifani, A. Allahham, *Opt. Laser Technol.* **90**, 174 (2017).
- [18] M. H. B. Stiddard, *J. Chem. Soc. Vol.* **0**, 4712 (1962). DOI: 10.1039/JR9620004712
- [19] J. Tory, B. Setterfield-Price, R. A. W. Dryfe, Frantisek Hartl, *Chem. Electro Chem.* **2**, 213 (2015).
- [20] M. D. Zidan, A. Arfan, A. Allahham, *Opt. Laser Technol.* **86**, 79 (2016).
- [21] N. K. Siji Narendran, R. Soman, C. Arunkumar, K. Chandrasekharan, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **136**, 838 (2015).
- [22] F. Nasser, E. Rokhsat, D. Dorranean, *Optik* **127**, 6813 (2016).
- [23] M. Gantenbein, Terminally diisocyno functionalized and rotationally restricted biphenyl systems, M.Sc. Thesis, Switzerland, University of Basel, 2010.
- [24] S. Pramodini, P. Poornesh, *Opt. Laser Technol.* **62**, 12 (2014).
- [25] F. Z. Henari, P. S. Patil, *Opt. Photonics Journal* **4**, 182 (2014).
- [26] S. Zafar, Z. H. Khan, M. S. Khan, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **114**, 164 (2013).
- [27] F. Z. Henari, W. J. Blau, *Proc. SPIE* **2854**, 174 (1996).
- [28] H. L. Saadon, B. Ali, A. A. Al-Fregi, *Opt. Laser Technol.* **58**, 33 (2014).
- [29] S. Pramodini, P. Poornesh, Y.N. Sudhakar, M. Selva Kumar, *Opt. Commun.* **293**, 125 (2013).
- [30] I. Papagiannouli, K. Iliopoulos, D. Gindre, B. Sahraoui, O. Krupka, V. Smokal, A. Kolendo, S. Couris, *Chem. Phys. Lett.* **554**, 107 (2012).
- [31] M. D. Zidan, A. Arfan, A. Allahham, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **190**, 135 (2018).
- [32] S. Wang, W. Huang, T. Zhang, H. Yang, Q. Gong, Y. Okuma, M. Horikiri, Y. F. Miura, *Appl. Phys. Lett.* **75**, 1845 (1999).
- [33] I. Guezguez, A. Ayadi, K. Ordon, K. Iliopoulos, D. G. Branzea, A. Migalska-Zalas, M. Makowska-Janusik, Ab. El-Ghayoury, B. Sahraoui, *J. Phys. Chem. C* **118**, 7545 (2014).

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