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Polarizability and Hyperpolarizability of Schiff Base Salen-H2 as Judged as UV-vis Spectroscopy and Simulation Analysis

Yasaman Abed[*,1], **Fatemeh Mostaghni**[2]
[1] Department of Physic, Payam Noor University, P.O.Box: 19395-4697, Iran
[2] Department of Chemistry, Payam Noor University, P.O.Box: 19395-4697, Iran

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Abstract: The aim of the present study was to evaluate the properties of linear and nonlinear optics of the Schiff base Salen. Crystal structure of nanoparticles was determined by a Bruker make diffractometer, Cu-Kα X-rays of wavelength (λ=1.5406 Å). The XRD patterns were recorded in the 2θ range of 10–90° with a step width of 0.02 s^{-1}. The UV-Vis Spectra recorded on a computerized double - beam Shimadzu 2550 spectrophotometer, using two matched 10.0 mm quartz cell. In this paper, refractive index, extinction coefficient and optical conductivity are calculated by using UV spectrum (Ultraviolet). Also, nonlinear optical property of matter and dielectric tensor are computed by using Gaussian software and based on density functional theory (DFT). The results showed that with decreasing of wavelength, the refractive index increase from 1.19 value to 2.64. This is due to the strong interaction between photons and conducting electrons. Also material was not asymptotic and has non-linear optical property, Also the triclinic structure for this material has been specified through dielectric tensor.

Key words: Dielectric Function, Dielectric Tensor, Non-Linear Optic

1. INTRODUCTION

Nowadays, many studies have been done on the nonlinear optical properties of materials [1]. Because non-linear optical (NLO) matters perform essential role in the technology of making optical keys, optical signal processing and optical limiters [2]. The type of nonlinear behavior in each material varies according to the atomic structure and composition. Different processes may cause non-linear responses in optical materials. However, the organic materials have a greater NLO properties than mineral compounds because of high and unique polarization of organic compounds, caused by extensive conjugated π systems.

Resistance of organic matters in compare to mineral is considerable in the exposure of strong laser beams. NLO organic molecules possess a strong donor-

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[*] Corresponding author. E-mail: **yabed203@gmail.com**

acceptor intermolecular interaction due to the presence of easily polarizable delocalized π -electrons in the system [3-6]. A large number of organic materials have been found to exhibit NLO properties [7-9].

Further research on organic materials with excellent nonlinear optical properties and vigorous application has been carried out. Among organic compounds, azo dyes have also attracted attention due to their potential applications in many aspects.

When the material is exposed to the light radiation, the electrons travel from the valence bands (VBs) to the conduction bands (CBs). The decreasing trend of band gap (the energy gap between HOMO and LUMO) indicates that more number of free electrons is available for charge conduction [10-11].

The electronically excited state produced upon absorption of light has dipolar character that is stabilized relative to the ground state, thus the ground state absorbs light of lower energy than could be expected for an analogous molecule without the electron donating/withdrawing groups.

Moreover, Azo dyes can be readily prepared with a wide range of donor and acceptor groups in order to change its absorption band according to demands and lead to higher optical activity [12-14].

In this paper, we investigated the linear and nonlinear optical properties of the salen-H2 compound. First, the size of particle is calculated by XRD spectrum. Because the particle size plays an important role in the optical properties of the materials. In the following, the refractive Index, Extinction coefficient and dielectric coefficients are calculated by UV spectrum. By aiding of Gaussian software, this material has been simulated and the polarization tensor values have been computed for the first, second, and third order Polarizability.

2. METHOD

Crystal structure of nanoparticles was determined by a Bruker make diffractometer, Cu-K$_\alpha$ X-rays of wavelength (λ=1.5406 Å). The XRD patterns were recorded in the 2θ range of 10–90^o with a step width of 0.02 s^{-1}. The UV-Vis Spectra recorded on a computerized double-beam Shimadzu 2550 spectro photometer, using two matched 10.0 mm quartz cell. IR spectra were measured on FTIR-6300 spectrometer (KBr).

All quantum chemical calculations were carried out with the Gaussian program 09 [15], as basic program and Gaussian Viewer as graphical medium. The calculations of DFT were carried out by using the three B3LYP functional. The usual 6-31G basis set was employed in the DFT calculations.

A. Synthesis of Salen

Salen-H2 (Fig. 1) was synthesized by the method reported in the literature [16]. A solution of 0.01 mol of ethylene diamine in 15 ml of methanol was added to a solution of 0.02 mol of salicylic aldehyde in 15 ml of methanol. The reaction mixture was agitated and refluxed for about 4 to 5 hours with magnetic stirrer. The precipitate was filtered off and recrystallized from ethanol. Yield: 92.5%. m.p= 125-126 ºC. The obtained product characterized with FTIR (Fig. 2). Selected IR bands (KBr, cm-1): 3450 (OH); 1635s (C=N); 1576m (C=C); 1371m (C-N); 1283m (C-O); UV–Vis (DMSO): λmax=410 (nm).

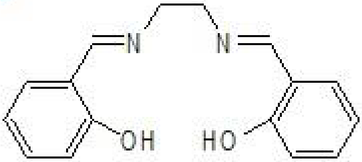

Fig. 1 SalenH2 or (*N*, *N′*-ethylenebis (salicylidene amine))

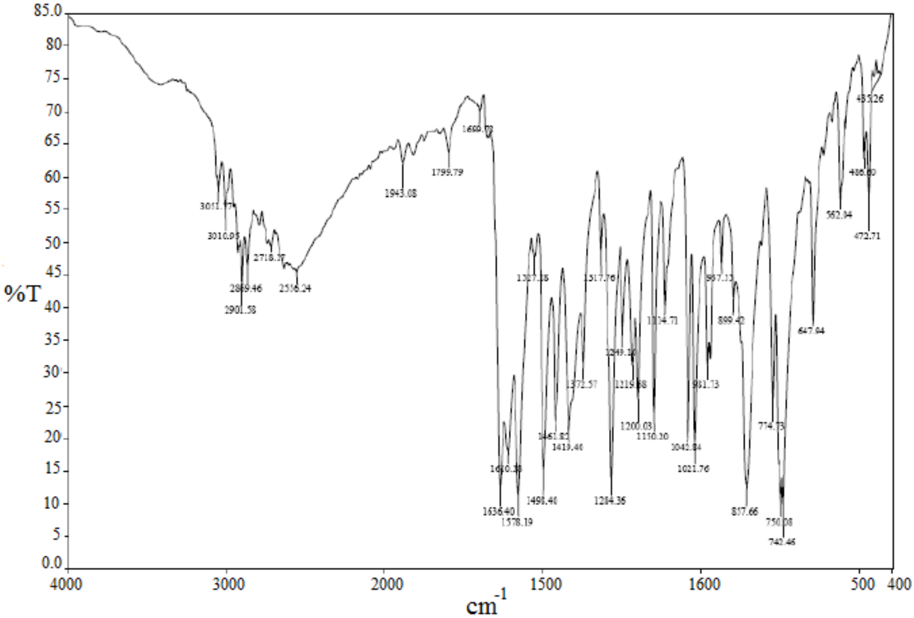

Fig. 2 The IR spectrum of synthesized salen

3. RESULTS AND DISCUSSION

A. Particles Sizes

The optical properties of a particle is related to its size. In nanoparticles, the distance between the electron-hole is controlled by particle size. As a result, with decreasing the size of the particle the density of states becomes more quantized and the absorption spectrum shows a blue shift [17]

The particle size has been calculated by using the scherrer equation (Eq. 1). Where D is the particles size and β is the width at half of the maximum. The calculated size through this method is equal to 30.56 nm. XRD spectrum is shown in Fig. 3.

$$D = \frac{K\lambda}{\beta cos\theta} \qquad (1)$$

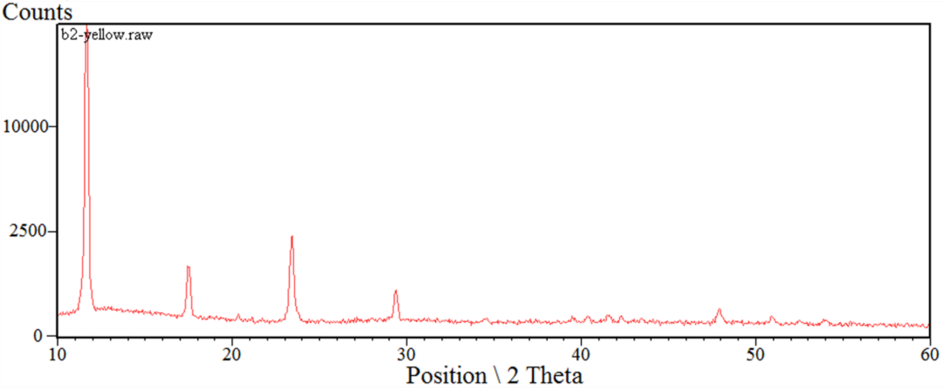

Fig.3 XRD Spectrum of ligand Schiff Base Salen

B. *Linear Optical properties*

The energy band gap of this compound is determined using the absorption spectra. According to the Taucc relation (Eq2) [18].

$$(\alpha h\nu) = \beta\left(h\nu - E_g\right)^{\frac{n}{2}} \qquad (2)$$

Where, α is the absorption coefficient, β is the absorption constant and E_g is the energy gap. The value of n for the indirect optical gap is 4. According to Fig.4, the indirect optical gap value is 2.2 ev. Whenever the particles size is small, the absorption spectrum shifts to smaller wavelengths.

According to the absorption spectrum, the extinction coefficient quantity k is computed from equation (3). This quantity is the criterion of Photon absorption rate in matter [19].

$$K = \frac{\alpha\lambda}{4\pi} \qquad (3)$$

Where α is the absorption coefficient. Fig. 5, shows the extinction coefficient in the absorption edge increases because of the strong interaction between conduction electrons and incident photons. Maximum extinction coefficient is observed in 2.5 eV. The particle size has a significant effect on the Extinction coefficient. However with decreasing the size of the particles, the extinction coefficient goes toward the shorter wavelengths.

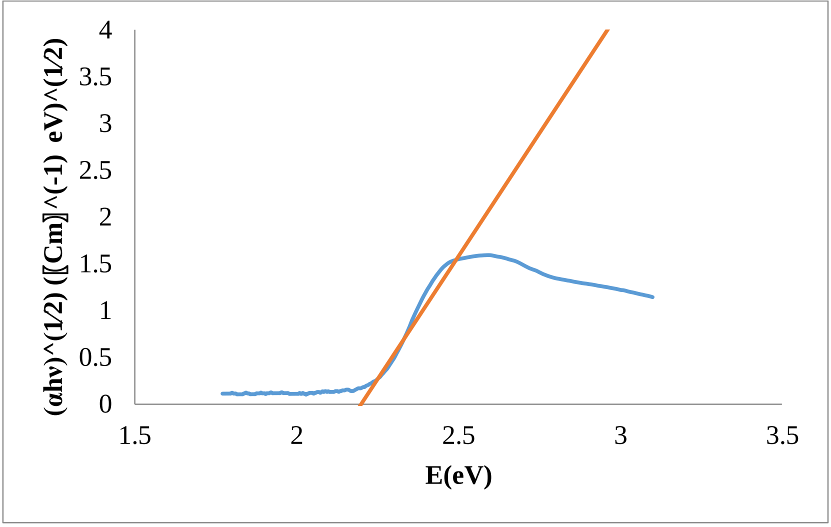

Fig. 4 Chart $(\alpha h\nu)^{1/2}$ based on E (eV)

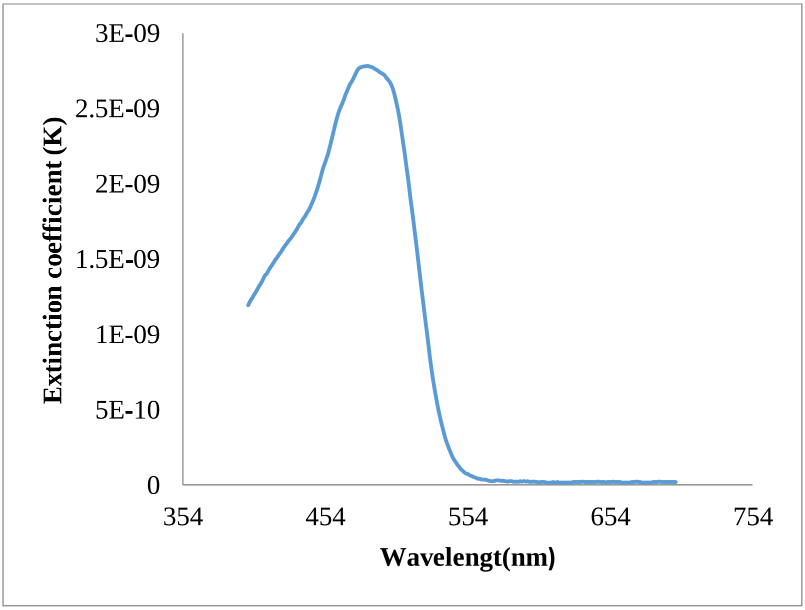

Fig. 5 Extinction Coefficient diagram based on wavelength

The refractive index n is the quantity used to indicate the reduction_of the light velocity in the environment relative to the vacuum which is calculated using the equation (4) [20].

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\left(\frac{4R}{(1-R)^2} - K^2\right)} \quad (4)$$

$$R = 1 - (A + T) \quad (5)$$

Where A is the absorption value, T is the transmittance and R is the light reflection rate (equation.5).

The particle refractive index varies in different wavelengths. At high wavelengths (transparent region), the refraction coefficient decreases. In short wavelengths (absorption region), the refractive index increases. As can be seen in Fig. 6, maximum refractive index observed in λ=525 nm.

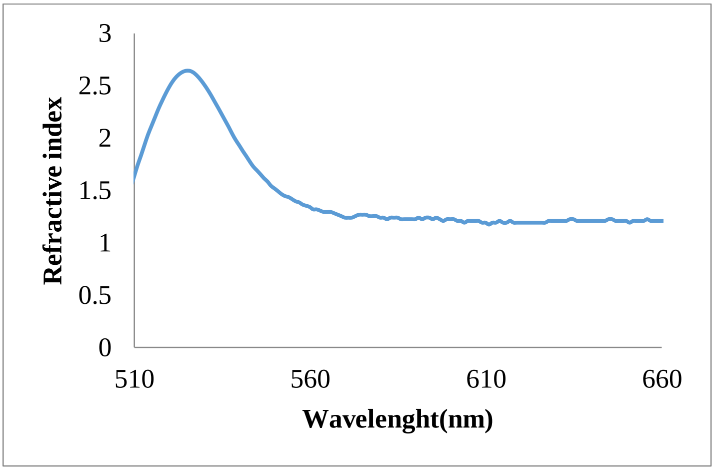

Fig. 6 Refraction coefficient diagram based on wavelength

The dielectric constant is one of the important parameters in the optical properties of materials. This parameter is used for materials_get polarized when placed in the electric field. This parameter is the response of a system to external electromagnetic fields which is radiated to it.

The dielectric constant has both real and imaginary parts, in which the real part is calculated from the equation (5) [21].

$$\varepsilon_r = n^2 - K^2 \quad (5)$$

The real part of the dielectric coefficient is shown in Fig. 7. Since $\varepsilon_r>0$, it is clear that our material is transparent and its absorption is very low in the region of 530 to 700 nm.

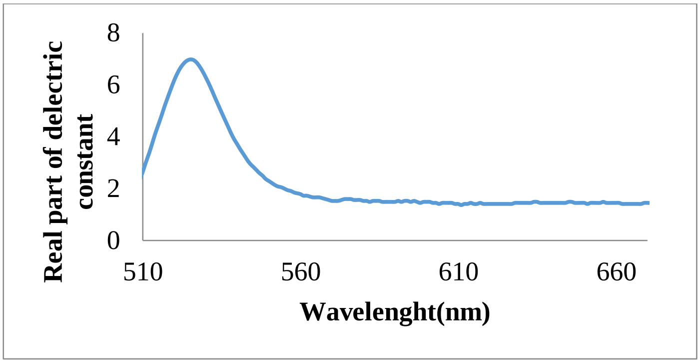

Fig. 7 The real part of the dielectric function

The imaginary part of the dielectric function is calculated from equation (6) [22], and is shown in Fig. 8.

$$\varepsilon_i = 2nK \tag{6}$$

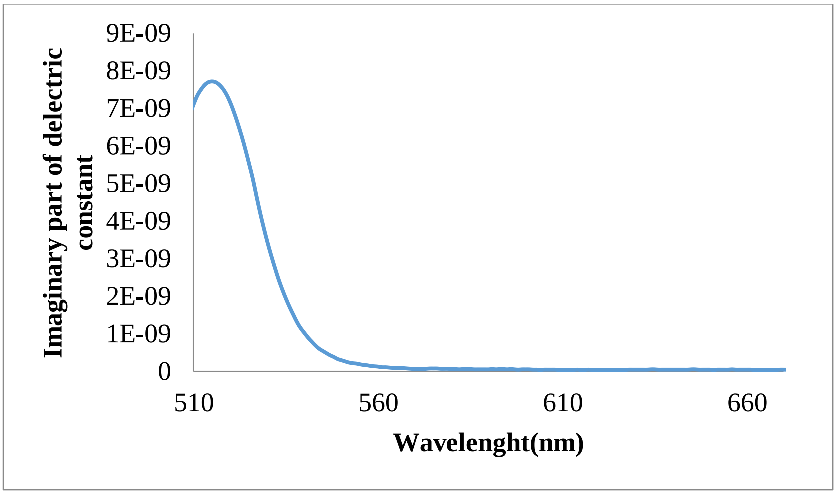

Fig. 8 The imaginary part of the refractive coefficient

In the transparent region, the real and imaginary parts of the dielectric constant are almost constant. But in the absorption region at short wavelengths, because of the strong interaction between the photon and electron, the dielectric constant increases and the variation is high. The polarization property of this ligand is seen in short wavelength region, as a result, this material can be used in short wavelengths to create polarized beams. The peak observed in the imaginary part of dielectric function means that the maximum transition in particular energies occurs.

Another parameter that is studied in the optical properties of a material is the conductivity coefficient that its value is calculated from equation (7) where C is the speed of light, α is the absorption coefficient and n is the refractive coefficient [23].

$$\sigma = \frac{\alpha n c}{4\pi} \tag{7}$$

The conductivity diagram for Schiff base salen is shown in Fig. 9. Based on Fig. 9, the conductivity increases at short wavelengths. For energies higher than 2.2 eV, the conductivity increases exponentially which is in consistent to the energy gap. Electrons with energy of less than 2.2 eV cannot reach the conduction band, But as soon as the time the energy of the photon get higher than 2.2 eV, the excitement takes place in unoccupied states and the excitation rate grows by increasing the energy of incident photons. This property of matter is used to make optical fiber for data transmission purposes.

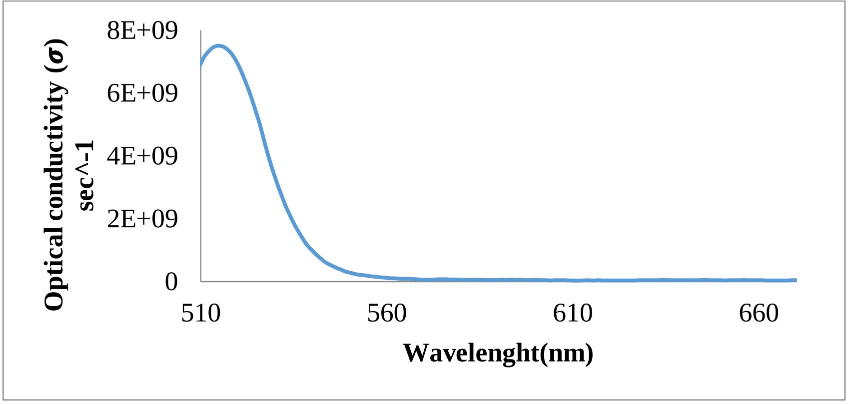

Fig. 9 Optical conductivity (σ)

C. Nonlinear Optics

When the material is exposed to light radiation, the exogenous electrons of the substance begin to oscillate. These oscillates attend with electromagnetism radiation and results in polarization of matter by external electric field (E_{ext}) [24]. For small magnitudes of E_{ext} polarization (P) is linear but deviate slightly from linearity as E_{ext} increase. Total polarization (P) for macroscopic system can be written

$$\chi = \chi^{1} E + \chi^{2} E^2 + \chi^{3} E^3 \tag{8}$$

Where the value $\chi^{(1)}$ is linear susceptibility, the proportionality coefficients $\chi^{(2)}$, $\chi^{(3)}$ and so on represent the higher order susceptibilities. Based on the above equation, the polarization is as follows:

$$P = \varepsilon_0 \left(\chi^{1} E + \chi^{2} E^2 + \chi^{3} E^{\ 3}\right) \tag{9}$$

The first term is the linear polarization and the second and third ones are the nonlinear response of the material relative to the field E_{ext}. In this paper, by using Gussian software and with the DFT method, the first, second and the third order polarization are calculated for this compound.

The main diagonal elements represent the permeability of the environment [25]. The non-diagonal elements relate to application of external magnetic field and are zero in the absence of external field since the calculated values for the tensor are real and symmetric, we conclude_that the matter is non-magnetic and has a triclinic structure. In addition, due to the non-zero values of the non-diagonal elements in dielectric tensor we find that this material is anisotropic.

For a microscopy system, total polarization can be written

$$P=\alpha E+\beta E^2+\gamma E^3 \tag{10}$$

Where α is first-order polarization tensor, β is first hyperpolarizability tensor and γ is second hyperpolarizability tensor.The first order polarization tensor is listed in Table 1.

TABLE 1

First order tensor elements

α_{xx}(a.u)	α_{yy}(a.u)	α_{zz}(a.u)	α_{xy}(a.u)	α_{xz}(a.u)	α_{yz}(a.u)
-90.9429	-106.5229	-119.2494	2.052	1.9610	3.5691

The average polarizability (α_{avg}) and anisotropy are obtained by the following equation and the values are listed in Table 2 [25].

$$\langle\alpha\rangle=\frac{1}{3}\left(\alpha_{xx}+\alpha_{yy}+\alpha_{zz}\right) \tag{11}$$

$$\Delta\alpha=\frac{1}{2}\left(\left(\alpha_{xx}-\alpha_{yy}\right)^2+(\alpha_{xx}-\alpha_{zz})^2+\left(\alpha_{yy}-\alpha_{zz}\right)^2\right) \tag{12}$$

TABLE 2

Values (α) first order dipolmoment, Anisotropy (Δα)

First order dipolmoment((α))	Anisotropy (Δα)
-105.57 a.u	17.36 a.u

The calculated first hyperpolarizability (second-order susceptibility) tensor elements for salen are reported in Table 3. If the molecule or crystal is Centro symmetric then first hyperpolarizability (β)=0.

Since this tensor is non-zero, it can be said that the material has an asymmetrical crystalline form. And also with respect to the varied values of the β tensor, we can say this matter has_the condition of being piezoelectric. And as a result, this material can be used to produce a second harmonic [26-27].

The value of first hyper polarizability is affected by donor moieties and number of Nitrogen atoms and is in invert relation to the energy gap. [28-29]

The value of β_{total} increase with the decrease of ΔE_{H-L} for salen and ΔE_{H-L} =3.268eV.

TABLE 3

First hyperpolarizability β

First order dipolmoment((α))	Anisotropy ($\Delta\alpha$)
-105.57 a.u	17.36 a.u

Also, the second hyperpolarizability γ (third-order polarizability) tensor for this material has been calculated and is listed in Table 4.

TABLE 4

The second hyperpolarizability γ (third-order polarizability)

First order dipolmoment ((α))	Anisotropy ($\Delta\alpha$)
-105.57 a.u	17.36 a.u

According to the calculated values for second and third order tensors, the value of first hyper polarizability, and also the second hyper polarizability are calculated by the following equations and is listed in Table (5) [26-27].

$$\beta_{tot} = \left[\left(\beta_{xxx}+\beta_{xyy}+\beta_{xzz}\right)^2+\left(\beta_{yyy}+\beta_{yzz}+\beta_{yxx}\right)^2+\left(\beta_{zzz}+\beta_{zxx}+\beta_{zyy}\right)^2\right] \tag{13}$$

$$\langle\gamma\rangle = \frac{1}{5}\left[\gamma_{xxxx}+\gamma_{yyyy}+\gamma_{zzzz}+2\left(\gamma_{xxyy}+\gamma_{xxzz}+\gamma_{yyzz}\right)\right] \tag{14}$$

TABLE 5

First hyper polarizability and second hyperpolarizability values

First hyperpolarizability β_{tot}	Second hyperpolarizability (γ)
179. 8 a.u	-4258.4 a.u

The conversion coefficients are as follows:
$Polarizability(\alpha) = 1\ au = 0.148176 \times 10^{-2} esu$
$First$ hyperpolarizability (β) = 1 au = 0.863993 × 10^{-32}esu
$second\ hyperpolarizability\ (\gamma) = 1\ au = 0.503717 \times 10^{-39} esu$

4. CONCLUSION

In this paper, we investigate the linear and nonlinear optical properties of the salen-H2 due to the presence of easily polarizable delocalized π -electrons in the system. According to the calculated UV spectrum of this compound, we found that its polarization property belongs to short wavelengths and consequently can be used to produce polar beams in short wavelengths. Also orbital-molecular calculations show non-linear orbital property of this compound that can be used as NLO. Since the β values is non-zero, salen has the condition of being piezoelectric and can be used for producing second harmonic. Since the electric susceptibility depends on microscopic structure of the environment, by using dielectric tensor, it is determined that the structure of this material is Triclinic.

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