Electronic Transfers and (NLO) Properties Predicted by AB Initio Methods with Prove Experimentally

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Abstract

Hartree-Fock (HF) method relies in the calculations of nonlinear optical properties (NLO) for benzoic acid molecule. Also, another theoretical study is conducted by using the TD-DFT Density Functional Theory through B3LYP/High Base Set 6-311++G (2d,2p) on Gaussian program09. Moreover, an experimental study has been done to obtain the electrons spectrum for benzoic acid with and without ethanol. While the experimental study is done by using UV/VIS. spectrophotometer. Energy gap values of electronic transition between HOMO and LUMO is obtained from theoretical and experimental results. Consequently, the theoretical result for determining the energy gap calculated from EHOMO-LUMO wasvery close to the results of UV / VIS. spectrum. A theoretical method is considered extremely appropriate towards compounds capable of absorbing in vacuum UV.

Key Words: HF, TD-DFT, UV/VIS, NLO, Benzoic Acid.

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Introduction

Over the last two centuries, there has been extensive study of molecular materials with nonlinear square optical interaction (NLO) in the electromagnetic field [1–14]. Where the systems like this, properties of NLO are commonly correlated with linear polarizability (α), second-order hyperpolarizability (β) and third-order hyperpolarizability (c) that mainly derived from p-conjugated donor-acceptor groups [15–20]. Nonlinear optical (NLO) parameters, that determine the molecules, reactivity, have enough reasons to consider it as one of the main advantageous systems due to the ease of industrialization [21–23] and flexibility of structure [24].

Tuning at the molecular level of the electronic properties offer of such systems their capability in the optoelectronics same As an electronic mechanism for optical measurement or high density optical [25–27]. Not long ago, the topic of The subject of molecular switching was fascinating in science, varying from biological process modeling to molecular electronic device design [28–32]. Quantum mechanics calculations are theory arithmetic equations designed as programming languages, which is successfully used to predict cloning energies, repeat molecular structures and interpret chemical reactions [33-36].

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TD-DFT, as a fundamental method, effectively employed to predicts a wide variety of molecular characteristics such as molecular weight infrastructure, vibration frequencies and energy atomization, energy and electrical ionization [37-40]. The energy gap in a semiconductor represented by the distance between equivalent band and the conductance band, while the other materials it represented by difference between MO [41]. There are two kinds of spectroscopy spectra, a molecule undergoes a shift from a high energy level to a reduced energy level emitting excess energy as a photon, and the radiations are come across in absorption spectroscopy as radiation losing the number of frequencies [42]. There was an important limit known as selection rule; the first typeis spin selection rule which happens during the electronic transition with no change in spin inversion. While the second type is Laporte selection rule that related to molecules that have a center of symmetry. [43-45]. The chemical structure of any molecule iIn the electronic state of excitement is totally unlike The ground-state system. Franck–Condon principle stated the electronic switch: transition is happening mostly with no changes in the molecular structure of the nuclei, and the nature of structure [46]. When a molecule transitions from a gas phase to a solvent state, wavelength and absorption intensity are affected, it is related to an unequal turmoil of the excited and ground the molecule states. It relies on the kind of interactions Between solvents and solutes at these states, but the absorption spectra in highly non-polar solvents keep almost the same characters of the gas phase spectra [47-48]

Calculation Method

Benzoic acid 3d module was built Use the application Gaussian View. The equilibrium geometries of structures were calculated with version 09 Gaussian package[49], and their corresponding geometries in the gas phase were fully optimized using (TD DFT) the three-parameter utilitarian Beckes and the useful connection of Lee, Yang and Parr (B3LYP) with the hypothesis level 6-311++G (2d, 2p) in vacuum and ethanol [50-51]. Some parameters of the quantum chemical have investigated Nonlinear optical properties (NLO) of benzoic in a vacuum used HF method. These parameters of quantum mechanism are the energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy of ionization (IE), affinity of electrons (EA), energy gap (E_{GAP}), absolute hardness (A), absolute softness (S), absolute electro negativity (χ), chemical potential (CP), additional electronic charges (_N_{Max}) and polarizability (α), and the first hyperpolarizability (β_o) [52-53]. Moreover, Urea was used to assess the NLO properties, and quantum chemical The parameters of urea were compared. In this operation, the findings have been taken from E_{HOMO} and E_{LUMO} without changing. The calculations were done by Equations 1-13.

$$\textbf{IE (Ionization Energy)} = -E_{HOMO} \quad \text{......} \quad (1)$$

$$\textbf{EA (Electron Affinity)} = -E_{LUMO} \quad \text{......} \quad (2)$$

$$Egap = E_{LUMO} - E_{HOMO} \quad \text{......} \quad (3)$$

$$\eta \ \textbf{(Hardness)} = (IE-EA)/\ 2 \quad \text{......} \quad (4)$$

$$S \ \textbf{(global softness)} = 1/\ \eta \quad \text{......} \quad (5)$$

$$So = 1/\ Egap \quad \text{......} \quad (6)$$

$$\chi \ \textbf{(Electronegativity)} = -\mu = -(\partial E/\partial \Lambda)\nu(\rho) = (IE+EA)/2 \quad \text{......} \quad (7)$$

$$CP = -\ \chi \quad \text{......} \quad (8)$$

$$\textbf{Global electrophilicity index } (\omega) = (-x)^2/2\eta = \mu^2/2\eta \quad \text{......} \quad (9)$$

$$N_{Max} = -\ CP/\ \eta \quad \text{......} \quad (10)$$

$$N = 1/\ \omega \quad \text{......} \quad (11)$$

$$\alpha \ \textbf{(Polarizability)} = 1/3(\alpha_{xx}+\alpha_{yy}+\alpha_{zz}) \quad \text{......} \quad (12)$$

$$\beta_o \ \textbf{(hyperpolarizability)} = [(\beta_{xxx}+\beta_{xyy}+\beta_{xzz})^2+(\beta_{yyy}+\beta_{yzz}+\beta_{yxx})^2+(\beta_{zzz}+\beta_{zxx}+\beta_{zyy})^2 \quad \text{......} \quad (13)$$

Whereas α_{xx} is the polarizability in the x-axis direction, α_{yy} is the polarizability in the y-axis direction, α_{zz} is the polarizabilityin the z-axis direction. β_{xxx},β_{yyy} and β_{zzz} are the hyperpolarizability in x, y, z-axis, respectively.

UV-Vis Measurements

Benzoic acid spectra are measured in

spectrophotometer device type (sp-3000 Nano). The mixture of benzoic acid and ethanol was measured under the same conditions. The order was introduced to the device like the range of wavelength scan (190-800 nm) and to subtract the λ_{max}. Water was used as blank with both benzoic acid solution and the mixture.

Theoretical Results and Discussion

Optical devices and telecommunications, investigations of nonlinear optical (NLO) properties are so important. Electron delocalization and molecule planarity improve the molecule's NLO characteristics. Computational methods can readily investigate NLO characteristics. In calculation there was no solvent effect; however, consideration should be given to the determination of NLO characteristics of the benzoic acid molecule. The calculation of specific parameters is done to investigate the characteristics of the NLO (Table 1). In these inquiries, Urea NLO parameters are used as a reference; therefore, it optimized at the same theory stage and the same QCDs and provided in the same table.

Table 1. Quantum mechanism parameters to investigate NLO properties

prodrug	E_{HOMO}^{a}	E_{LUMO}^{a}	IE^{a}	EA^{a}	E_{gap}^{a}	η^{a}	S^{b}	So^{b}
Benz.	0.484	-9.782	9.782	-0.484	10.266	5.133	0.194	0.097
Urea	-6.727	1.559	9.522	-1.559	8.286	2.633	0.380	0.121

	χ^{a}	CP^{a}	ω	N_{Max}	α^{c}	β_{o}^{d}
Benz.	4.649	-4.649	2.105	0.905	1.597	13.683*10^{-35}
Urea	6.889	-6.889	0.805	2.616	2.153	3.13*10^{-28}

ain eV, b in eV-1,c in Å3, d in cm5/esu.

QCDs are advantageous by determining the molecule activity, and the only benzoic acid molecule is given by these parameters. The first descriptor to examine is HOMO's power. If HOMO's power level is high, HOMO's electrons move faster and can pass to higher concentrations. Due to NLO molecule activity rises the electron mobility rises too. Along side, NLO molecule characteristics rise by the growing HOMO's energy level. As stated by the NLO classification of the HOMO energy level must be as follows:
Benz. > Urea
LUMO's energy is the second parameter. LUMO's lower energy level means that LUMO's electrons can easily be inhabited. Hence, molecular NLO activity increases as the LUMO energy level decreases. NLO activity rankings must be according to the LUMO energy level:
Benz. > Urea
The third parameter is represented by the energy gap between LUMO and HOMO. By reducing the energy between implies increasing a mobility of electrons, this promotes the rise of NLO:
Urea > Benz.
The chemical hardness and softness are the fourth and fifth parameters. The increase of chemical softness
Urea > Benz.

Alternatively, decreasing chemical hardness means enhancing molecular polarization. The correlation between the activity of polarizability and NLO is directly proportional. The NLO activity ranking should be the following in terms of these explanations:
Urea > Benz.
Optical softness is the fifth parameter of NLO activity determination. The increase in optical softness implies that the NLO characteristics are increasing. The ranking of NLO activities should be:
Urea > Benz.
The sixth parameter is the absolute electro negativity and chemical potential. With a reduced absolute electro negativity electron delocalization improves. There is also a direct correlation between the activity of NLOs and the chemical potential. The NLO activity of the compound should be followed according to this parameter:
Benz. > Urea
A further electronic charge is the seventh parameter. Electronic charging is associated with molecular polarizability. The higher value for NLO apps is more active. The NLO activity of the molecule should be followed according to this parameter:
Urea > Benz.
The final parameters are molecule polarizability and hyperpolarizability. With the rise of the listed

descriptors, the NLO characteristics improve. The ranking of NLO activity should be:
Urea > Benz. (α)
Urea > Benz. (βo)
As stated by the above ranking, the compound's NLO properties area little better than urea, and it's a good candidate for applications for NLO.

Theoretical Electronic Spectra

Quantum chemical computations were employed to look intoelectronic properties of the compound studied. Calculations contain the electronic absorption spectra (UV-Vis), like the HOMO and LUMO, the energies of orbital. The energy gap ($E_g = E_{LUMO} - E_{HOMO}$), wavelengths of absorption (λ max), and oscillator strengths (f) based on an optimized geometry with water, and ethanol, **Table 2** and **Figures 1-2**. Frank – Condon principle, which determines maximum peak absorption in a UV–Vis., performs the calculations involving the vertical excitation energies

Theoretically, spectra for benzoic acid with water solvent in **Figure 1**showed two peaks first at (215 nm) for π-π*, and second for n- π* at (264 nm), while the energy gap equal to (5.7 eV). The second part calculations with ethanol. The effect of ethanol as shown in **Figure 2** two peaks first at (194 nm) for π-π*, and second for n- π* at (231 nm), while the energy gap equal to (5.9 eV) due to decrease the π* level of the polar effect. The calculations contain the electronic absorption spectra (UV-Visible), to calculate the energy gap in equation 14, such as HOMO and LUMO orbital energy:

$$E_g = E_{LUMO} - E_{HOMO} \tag{14}$$

and from spectra by using equation 15:

$$E = hC/\lambda \tag{15}$$

where (h= blank constant, c= speed of light, λ= greater wavelength

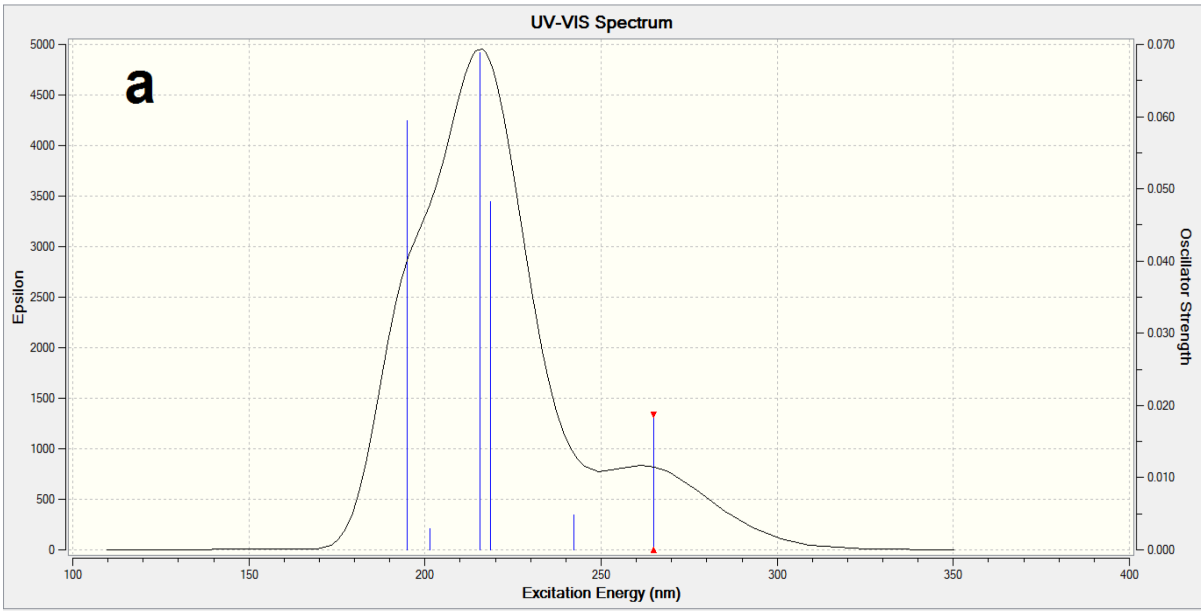

Figure 1. Charts showing lambda max and other absorption for benzoic acid solution theoretically by (TD-DFT)

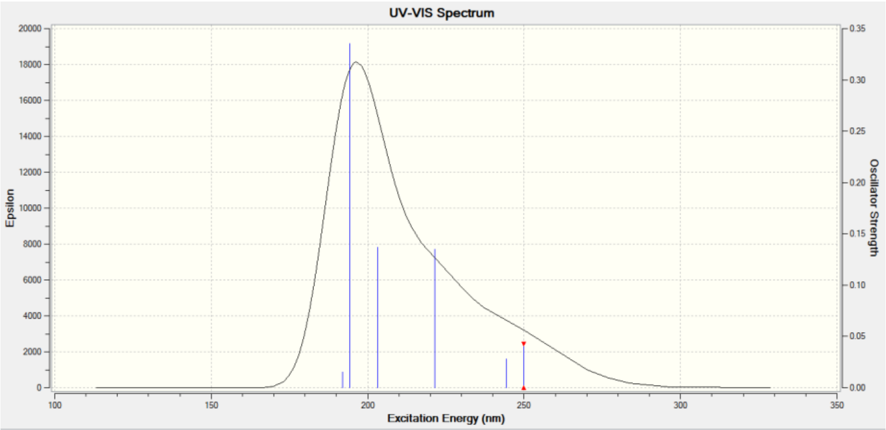

Figure 2. Charts showing lambda max and other absorption for the benzoic acid solution with ethanol theoretically by (TD-DFT)

Table 2. Theoretical results for the benzoic acid solution and ethanol studied.

Com. Name	Theoretical Results				
	π-π^*	n- π^*	$\Delta E_{LUMO-HOMO}$	E=hc/λ	f
Benzoic acid with water	215	264	5.77	5.76	0.0187
Benzoic acid with ethanol	194	231	5.92	6.39	0.134

Experimental Results

UV-VIS spectroscopy was used firstly as a method in this way by one of the pioneers Pedersen [54].The curve of UV absorbance of benzoic acid in water as solvent shows two peaks, the first one is π-π^* at (220 nm) and second at (270 nm) n- π^* for non-bonding oxygen electrons and the aromatic ring respectively, **Table 2**. The actual lambda max represents the first transition due to the uniform shape of π levels. While the benzoic acid solution with polar effect (ethanol) shifted the peaks to low wavelength. The first peak at (215 nm) for π-π^* whereas the π^* level will tend to dawn. The second peak present at (255 nm) to n-π^* due to polar effect, in addition to the possibility of hydrogen bonds forming **Table 3**.

Table 3. Experimental results for the benzoic acid solution and ethanol studied

Com. Name	Experimental Results		
	π-π^*	n- π^*	E=hc/λ
Benzoic acid with water	220 nm	270 nm	5.6
Benzoic acid with ethanol	215 nm	255 nm	5.7

Conclusion

The quantum mechanics calculation of benzoic acid molecule presents the electrons transition, λ_{max}, oscillator strength, energy gap, and NLO properties. The electronic peaks predicted by **TD-DFT** of benzoic were shifted from **(215) to (194)** nm for π-π^* and **(264) to (234)** nm for n-π^* in ethanol. The compound measured experimentally by spectrophotometer device that described the electrons transition, and λ_{max}, in addition to the comparison between theoretically and experimentally results showed by coefficient determination value and their convergence.

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