



A Study of the Nonlinear Optical Properties of Stilbazolium Derivative Crystal

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Abstract. In this report we start from *ab initio* calculations to get the structural properties of an isolated molecule of an organic crystal. Since the knowledge of the effects of neighboring molecules their study became necessary for an appropriated description of nonlinear optical properties in the solid state and more efficient design of such materials requires theoretical models that describes in detail the structural and electronic properties of the crystalline environment. The derivative of an organic stilbazolium single crystal, (E)-1-ethyl-2-(4-nitrostyryl) pyridin-1-ium iodide (NSPI); the NSPI crystallizes in the centric triclinic system with the $P\bar{1}$ space group. Here the dipole moment, the linear polarizability, and second hyper polarizability of the asymmetric unit of the compound were investigated through a super molecule approach in combination with an iterative scheme. In this approach the electrostatic interactions of the atoms of molecules embedded are represented by point charges. In addition to these calculations, other interesting results are obtained when we compare the results for isolated molecule and the molecule under the influence of its crystalline environment (embedded molecule); under such an influence we find a very interesting result for the average 2nd hyperpolarizability: 290,000% higher in the isolated molecule when compared to the embedded one.

Keywords. Molecule embedded; 2nd hyperpolarizability; Dipole moment; Linear polarizability; Supermolecule approach

PACS. 73.22.-f; 78.67.Bf; 42.70.Mp; 42.70.Nq

Received: May 4, 2020

Accepted: June 26, 2020

1. Introduction

Nowadays, the use of organic materials as *nonlinear optical* (NLO) materials has gained great motivation for its easy handling in the laboratory, allowing us to control the NLO properties of the material [1]. Studies involving nonlinear optical processes, mainly with light [2–8], contribute immensely to the development of photonics [9, 10], electro-optic modulators [11], spectroscopy [12, 13], frequency converters [14], optical switches [15], fiber optic lines [12], data transmission network so on and so forth [16], and still in considerable applications in the health area [17–19]. The compounds that exhibit a high non-linearity are of enormous interest in the area of non-linear optics, since they integrate the composition of devices that reach high speed [16, 20].

Quantum mechanics calculations were used to obtain the electrical properties of the asymmetric unit. Nonetheless, when working with organic crystals, we must consider the effects of the neighboring molecules to estimate a better characterization of the *nonlinear optical properties* (NLO) of solid state materials. This stems from the fact that, organic crystals are normally very large and the characterization of their properties requires the use of theoretical models that involve quantum mechanics to represent the mechanical and electronic properties of the crystalline environment in which the molecules are introduced [21, 22]. Organic crystals with nonlinear optical properties are of great relevance for electronics devices and for other applications in the field of materials science. For example, a nonlinear organic crystal used in hybrid systems may allow to control the quantum states previously prepared for use in these electronic devices. In this line the Kerr effect (χ^3), as well as other nonlinear effects of higher order, e.g., (χ^5), has been comprehensively used in scientific research laboratories [23–25].

The hyperpolarizabilities and polarizabilities discriminate the degree of distortion of the molecular electronic cloud due to an application of an external electric field that varies or not with the frequency. To pursue this line of research, it is important to get a deeper understanding of long-range intermolecular dispersion and induction forces.

This work aims to study the NLO properties in the static and dynamic case of crystal (E)-1-ethyl-2-(4-nitrostyryl) pyridin-1-iodide [26] (NSPI), with molecular formula $C_{15}H_{15}IN_2O_2$, which is a derivative of stilbazolium crystal shown in Figure 1.

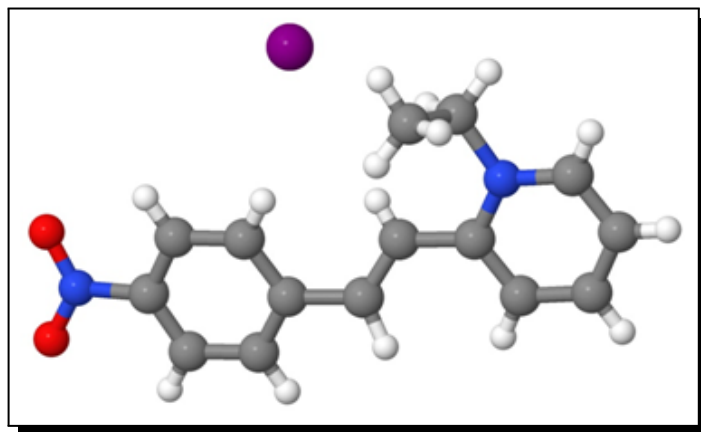


Figure 1. Asymmetric unit of NSPI

2. Material and Methods

The *supermolecule* (SM) approach [27–36] is used in an iterative process where we simulate the polarization effect of the medium on the electrical properties of the mentioned molecule [32]. This procedure takes into account the dominant intermolecular interactions that are electrostatic in nature and takes into consideration the long-range electrostatic effects. The relevancy of this approach, concerning the electrostatic incorporation, is supported by the rapid convergence of the dipole moment of the crystal throughout the iterative process, the same being valid for the electrical properties such as total dipole moment, linear polarizability, first and second hyper polarizabilities.

To determine this method, the experimental geometry of the NSPI asymmetric unit was used. A bulk was built with 286,720 atoms of the NSPI compound. This configuration was used as it is the smallest in which the convergence of the electrical properties studied in this work is obtained.

For the calculation of linear polarizability and dipole moment values, we used MP2 and DFT/CAM-B3LYP for the second hyperpolarizability. For atoms H, C, O and N, we use the basis set 6-311+G(d) and for iodine we use the pseudo potential LANL2DZ. The super molecule approach was used to calculate the charges from an electrostatic ChelpG assembly. These charges were placed at the positions of the atoms that circulate the asymmetric unit of the compound NSPI making up the bulk. Then another calculation was performed, now in the presence of this electrostatic incorporation to obtain the values of the new atomic charge and this procedure was repeated until the convergence of the total dipole moment is reached (see Figure 2).

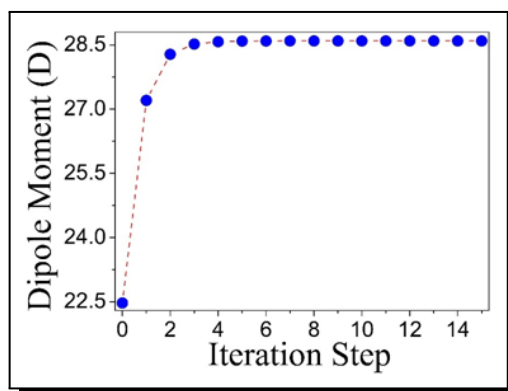


Figure 2. Convergence of dipole moment of super molecule approach used the set of base functions 6-311+G(d) in the level Møller-Plesset of second order - MP2

The applicability of the SM approach and the electrostatic interaction is based on the rapid convergence of the molecule's dipole moment (μ) along the iterative process of electronic polarization; this approach used here leads to results of dipole moment close to the experimental ones [32, 37] and the process begins with the atomic charges of the isolated molecule.

3. Results and Discussion

Using the set of base functions 6-311+G(d), the components and the total dipole moment, linear polarizability and second hyperpolarizability for the NSPI structure were calculated and the results are shown in Table 1, for the isolated structure.

Table 1. MP2 results for the components and the total dipole moment (D) and the average linear polarizability (in 10^{-24} esu) and CAM-B3LYP results for the second hyperpolarizability (in 10^{-36} esu) for NSPI isolated molecule

μ_x	μ_y	μ_z	μ			
13.11	-2.75	-18.05	22.47			
α_{xx}	α_{xy}	α_{yy}	α_{xz}	α_{yz}	α_{zz}	$\langle\alpha\rangle$
24.59	4.55	40.26	-11.70	-8.79	45.93	36.93
γ_{xxxx}	γ_{yyyy}	γ_{zzzz}	γ_{xxyy}	γ_{yyzz}	γ_{xxzz}	$\langle\gamma\rangle$
218.92	591.03	634.01	227.79	313.71	348.97	644.98

Table 2 shows the results for the NSPI embedded molecule. The results of the total dipole moment converge at 22.92D for the NSPI alone and 28.59D for the NSPI embedded molecule, revealing that the effects of polarization contribute to a 24.74% increase in comparison with the result of NSPI alone. Analyzing each component, the results obtained for NSPI isolated in relation to NSPI embedded molecule, a difference is obtained for μ_x of 24.79%, for μ_y of 20.36% and for μ_z of 28.64%, showing that the greatest influence of polarization affects the μ_z component. The average polarizability for the isolated NSPI is 36.93×10^{-24} esu and converges at 34.81×10^{-24} esu with the incorporation of charges, which reveals that the polarization effects contribute with a small decrease of 5.74% in relation to the isolated NSPI.

Table 2. MP2 results for the components and average values of the dipole moment (D) and linear polarizability (in 10^{-24} esu) and CAM-B3LYP results for the second hyperpolarizability (in 10^{-36} esu) for the NSPI embedded molecule

μ_x	μ_y	μ_z	μ			
16.36	-3.31	-23.22	28.59			
α_{xx}	α_{xy}	α_{yy}	α_{xz}	α_{yz}	α_{zz}	$\langle\alpha\rangle$
23.16	4.72	37.96	-10.65	-8.29	43.33	34.81
γ_{xxxx}	γ_{yyyy}	γ_{zzzz}	γ_{xxyy}	γ_{yyzz}	γ_{xxzz}	$\langle\gamma\rangle$
25.00	73.61	183.04	22.70	60.48	40.04	105.62

The values of the average second hyperpolarizability is 644.98×10^{-36} esu for the NSPI isolated molecule alone and converges at 105.62×10^{-36} esu for the NSPI embedded molecule, showing that the polarization effects contribute to an 83.62% decrease in embedded molecule when compared to the isolated NSPI.

By establishing a percentage comparison between the components of the NSPI, a difference between γ_{xxxx} and γ of 194.62%, γ_{yyyy} and γ of 9.13%, γ_{zzzz} and γ of 84.82% is obtained. For the NSPI embedded molecule, the difference between γ_{xxxx} and γ of 323.88%, γ_{yyyy} and γ of 43.49%, and for γ_{zzzz} and γ a decrease of 42.11% was observed; hence the component with the greatest contribution to the second average hyperpolarizability was γ_{yyyy} .

Again, analyzing each component, the results obtained for the NSPI alone in relation to the NSPI embedded molecule, a difference is obtained for γ_{xxxx} of -88.58% , for γ_{yyyy} of -87.55% , for γ_{zzzz} of -71.13% , showing that the greatest influence of polarization effects occurs on the γ_{xxxx} component.

4. Relating Dynamic Second Hyperpolarizability

The vibrational frequency-dependent of the second hyperpolarizability and its dynamic effects are presented in this topic. The values average second hyperpolarizability $\langle\gamma(-\omega; \omega, 0, 0)\rangle$ and $\langle\gamma(-2\omega; \omega, \omega, \omega)\rangle$ of the isolated and embedded molecule, for the frequencies $\omega = 0.0428$ a.u. and $\omega = 0.08$ a.u. are shown in Table 3.

Table 3. CAM-B3LYP/6-311+G(d) Results of components of the second hyperpolarizability, given in 10^{-36} esu

NSPI	$\omega = 0.0428$ a.u. $\lambda = 1064$ nm		$\omega = 0.08$ a.u. $\lambda = 569.5$ nm	
	$\langle\gamma(-\omega; \omega, 0, 0)\rangle$	$\langle\gamma(-2\omega; \omega, \omega, \omega)\rangle$	$\langle\gamma(-\omega; \omega, 0, 0)\rangle$	$\langle\gamma(-2\omega; \omega, \omega, \omega)\rangle$
Isolated	1546780	190983	-3958	1586
Embedded	130.23	237.47	282	-960

When we compare the value of the average second hyperpolarizability of the isolated NSPI molecule in the static case, with the dynamic cases $\langle\gamma(-\omega; \omega, 0, 0)\rangle$ and $\langle\gamma(-2\omega; \omega, \omega, \omega)\rangle$ for the frequency value of $\omega = 0.0428$ a.u., we observed an increase of $239,000\%$ and $29,000\%$, respectively. Meanwhile, the results for the NSPI embedded molecule are 22.89% and 124.09% , as shown in Table 3.

The highest value of the average second hyperpolarizability $\langle\gamma(-2\omega; \omega, \omega, \omega)\rangle$ was found for the frequency $\omega = 0.085$ a.u. for a NSPI isolated molecule. The linear polarizability dispersion curves of the isolated and embedded molecule are shown in Figure 3. The peaks found in Figure 3(b) and (c) refer to resonance or transition points.

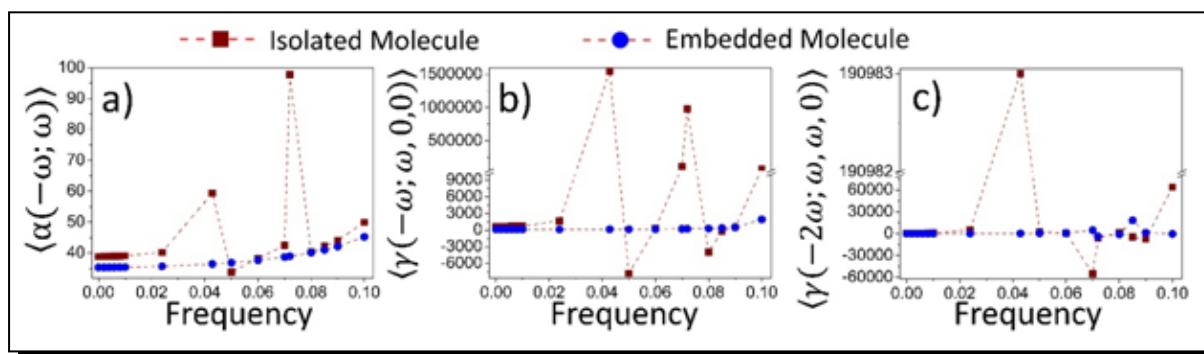


Figure 3. Dynamic evolution of the calculated values of the linear polarizability (in 10^{-24} esu) and second hyperpolarizability (in 10^{-36} esu) for NSPI ((a),(b),(c)) and with respective values of frequencies

5. Conclusion

In the present study we have used the SM approach in an iterative process where we reproduce the polarization effect of the medium on the electrical properties of the NSPI structure. The results of the second hyperpolarizability, of the total dipole moment, and the linear polarizability of the NSPI molecule were obtained and related to the isolated and embedded cases of NSPI. This model and the SM approach allows us to obtain results close to the experimental ones, but it is important to note that other (structural) factors of the molecule can also affect the properties of the crystalline environment, whose influences can cause changes in the NLO crystal and in the results of calculations.

The results of the total dipole moment and the average linear polarizability of NSPI embedded molecule were 2.75 and 7.57 times greater than the results of the urea [38], respectively [38–40]. The values for the average linear polarization converges at 36.93×10^{-24} esu for the isolated molecule and at 34.81×10^{-24} esu for the embedded molecule. The result of the second hyperpolarizability for the NSPI isolated molecule at 644.98×10^{-36} esu is 2.33 times greater than that reported in the literature [36].

The results obtained for the second hyperpolarizability are of great importance for the scientific community since the knowledge of these optical properties of materials can promote the advance in the manipulation of electronic optical devices. The results found from the second hyperpolarizability reveal that the molecule has properties with significant values, which implies a third order microscopic behavior. An outstanding result in this work is the increase of the second hyperpolarizability $\langle \gamma(-\omega; \omega, 0, 0) \rangle$ of more than 290,000% for the isolated NSPI molecule, in comparison with the value obtained in the case of NSPI embedded molecule. As a future perspective, the study of influences of different non-linear crystals on the behavior of optical devices deserves continued attention.

Acknowledgments

The authors wish to thank Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), the Fundação de Amparo à Pesquisa de Goiás (FAPEG), and the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for the financial supports. Also, the authors are grateful to the High Performance Computing Center of the Universidade Estadual de Goiás (UEG).

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

All the authors contributed significantly in writing this article. The authors read and approved the final manuscript.

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