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ORIGINAL PAPER

Second and third-order nonlinear optical behavior of natural pigment: chlorophyll and crocin

A. Karakas[1] · **M. Karakaya**[2] · **M. Taser**[1] · **Y. Ceylan**[1] · **A.K. Arof**[3] · **Y. El Kouari**[4] · **B. Sahraoui**[5]

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Abstract To provide an insight into the microscopic second and third-order nonlinear optical (NLO) behavior of chlorophyll *a* and crocin, we have computed the electric dipole moments (μ), dispersion-free first hyperpolarizabilities (β), frequency-dependent first and second (γ) hyperpolarizabilities at 1064 nm wavelength area using time-dependent Hartree-Fock (TDHF) method. According to ab-initio calculation results, the examined compounds exhibit first and second hyperpolarizabilities with non-zero values, implying second and third-order NLO phenomena.

Keywords Nonlinear optical properties · Electric dipole moment · First hyperpolarizability · Second hyperpolarizability · Time-dependent Hartree-Fock

Introduction

Quadratic nonlinear optical (NLO) behavior, due to its applications in optical communication and processing, has attracted interest of a large number of researchers in the search of materials with large microscopic and macroscopic NLO properties [1–5]. The compounds consisting of an electron donating and electron accepting group connected with a π -conjugated chain are of great interest [6]. The organometallic complexes rich in carbon and containing π -conjugated chains are materials interesting for the study of electronic transfer processes [7]. Significant interest exists in the design and development of materials exhibiting large second-order NLO response because of the potential application in telecommunications, optical computing, and optical signal processing [8]. The third-order response governed by the second hyperpolarizability offers more varied and richer behavior than the second-order NLO process due to the higher dimensionality of the frequency space. Using organic molecules for nonlinear media has several advantages, such as low cost, low dielectric constant, and the great diversity of possible organic structures [9]. Devices for applications in optical communications, optical processors, optical switches, wavelength filters, and modulators have been created using the NLO response properties of organic systems. The importance of these properties provides great motivation for the performance of high-level theoretical calculations. During the investigations for NLO, quantum chemical calculations have made an important contribution to the understanding of the hyperpolarizabilities underlying the molecular NLO processes and the establishment of structure-property relationships. For the free molecule, accurately determined experimental dipole and quadrupole moments, first and second hyperpolarizabilities are known and could be reproduced by ab-initio calculations, if reasonably high correlation levels and suitable basis sets were used [10]. On the other hand, the use of semiempirical methods to calculate the NLO properties has been less reliable due to the parametrization problems in the method of choice. However, the utilization of ab-initio methods to calculate the NLO

✉ A. Karakas
akarakas@selcuk.edu.tr

[1] Faculty of Sciences, Department of Physics, Selcuk University, Campus, Konya, Turkey

[2] Department of Energy Systems, Faculty of Engineering & Architecture, Sinop University, 57000 Sinop, Turkey

[3] Centre for Ionics University of Malaya, Physics Department, University of Malaya, 50603 Kuala Lumpur, Malaysia

[4] University Hassan II of Casablanca, Casablanca, Morocco

[5] CNRS UMR 6200, Laboratoire MOLTECH-Anjou, LUNAM Université, Université d'Angers, 2 Bd Lavoisier, 49045 Angers Cedex, France

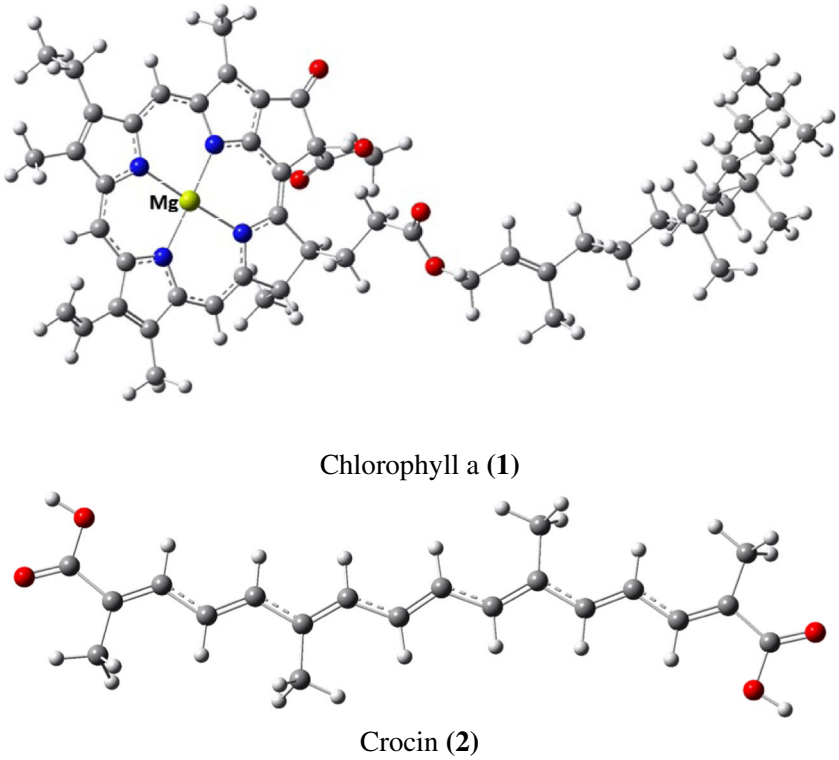

Fig. 1 Chemical structures of chlorophyll *a* (*1*) and crocin (*2*)

characteristics has been exploited less owing to the heavy computational cost. In spite of the rapid development of highly advanced experimental techniques on NLO, the theoretical understanding of the NLO properties shows that the responses of molecule to the external application of an electric field are also much important. It is known that there are several well-established computational procedures that include correlation at various levels of rigor and used for computation of NLO properties. The time-dependent Hartree-Fock (TDHF) is rather useful among the various computational procedures given the details in Ref. [11] to calculate the NLO properties of the compounds.

Theoretical calculations offer a quick and inexpensive way of predicting the NLO responses of the materials especially during the design of new materials. The present work aims to contribute to the knowledge of the electric properties of chlorophyll *a* (1) and crocin (2) (Fig. 1) by computing electric dipole moments, static quadratic β, dynamic β and cubic γ hyperpolarizability values. We present here a highly accurate ab-initio study utilizing TDHF procedure.

Theoretical calculations

The theoretical computations involve the determination of electric dipole moments, dispersion-free first hyperpolarizability, and frequency-dependent first and second hyperpolarizability tensor components. The molecule geometries of 1 and 2 have been firstly optimized. The geometry optimizations have been followed by the calculations of ground state dipole moments and hyperpolarizabilities with 6-31G(*d*) polarized basis set. Some computational codes tested are important as valuable theoretical tools used for computation of hyperpolarizabilities. Dispersions of hyperpolarizabilities have been frequently implemented at the self-consistent field level of theory (known as TDHF) [12]. $\beta(0;0,0)$ at $\omega = 0$ and $\beta(-\omega;\omega,0)$, $\gamma(-2\omega;\omega,\omega,0)$ calculations at $\omega = 0.04282$ atomic units (a.u.) (i.e. at $\lambda = 1064$ nm wavelength) have been carried out using the TDHF method with 6-31G(*d*) basis set implemented in the General Atomic and Molecular Electronic Structure System (GAMESS) [13] program. $\beta(0;0,0)$ above mentioned definition describes the static second-order hyperpolarizability. $\beta(-\omega;\omega,0)$ and $\gamma(-2\omega;\omega,\omega,0)$ computations at considered ω frequency were carried out by Electro-optic Pockels Effect (EOPE) and DC-Electric-Field-Induced Second Harmonic Generation (DC-EFISHG) groups, respectively, of the TDHF procedure.

Table 1 The ab-initio calculated electric dipole moments μ (Debye) and dipole moment components for 1–2

Compound	μ_x	μ_y	μ_z	μ
1	−0.465	0.513	−4.527	4.579
2	−0.151	−0.031	−0.001	0.154

Table 2 Some selected components of the static $\beta(0;0,0)$ and $\beta-V$ ($\times 10^{-30}$ esu) values for 1–2

Compound	β_{xxx}	β_{yyy}	β_{xxz}	β_{yzz}	β_{zzz}	β_x	β_y	β_z	$\beta-V$
1	2.682	8.447	−5.905	−12.485	10.370	2.376	3.032	−0.560	3.893
2	−3.861	0.013	−0.000	−0.014	0.001	−11.310	−1.077	−0.001	11.361

Many types of first hyperpolarizability computations have been discussed in the literature in the form of $\beta-V$ (β vector) which is the vector part of the first hyperpolarizability [14]. In this work, the $\beta-V$ [14] and the averaged (isotropic) third-order hyperpolarizability $\langle\gamma\rangle$ [15] values have been calculated using the following expressions:

$$\beta{-}V = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{1/2} \quad (1)$$

where $\beta_i (i = x, y, z)$ is given by:

$$\beta_i = (1/3) \sum_{j=x,y,z} \left(\beta_{ijj} + \beta_{jij} + \beta_{jji}\right) \quad (2)$$

$$\langle\gamma\rangle = (1/5)\left[\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\left(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz}\right)\right] \quad (3)$$

All electric dipole moment and hyperpolarizability calculations have been performed on a PC with an Intel (R) core (TM) I7-2630QM operator, 5.8 GB RAM memory and 2 GHz frequency using Linux PC GAMESS version running under Linux Fedora release 11 (Leonidas) environment.

Computational results and discussion

To study molecular structures and assemblies, NLO techniques are considered among most of structure-sensitive methods [16]. The calculations of quantum chemistry have been shown to be useful in the description of the relationship among the electronic structure of the systems and their NLO response [11, 17–19]. The determination and analysis of the NLO properties of molecular systems with theoretical methods have greatly progressed during the past years. Actually, to accurately compute NLO properties of molecular systems, there are well-tested computational codes. In particular, an accurate analysis of the NLO behavior leads to the definition of second and third-order hyperpolarizability values. Once conceived, the idea can be first pursued by theoretical means, and promising results would justify experimental efforts to obtain the envisioned compounds synthetically as well. One could determine the hyperpolarizability tensors of molecules using a suitable computational approach. These tensors describe the response of molecules to an external electric field. At the molecular level, the NLO properties are determined by their dynamic hyperpolarizabilities. TDHF is a procedure generally used to find out approximate values and can be a means of understanding both static and dynamic hyperpolarizabilities of molecular structures. We present here an ab-initio study on the NLO properties of the title compounds using the TDHF method. In this study, in addition to the static first hyperpolarizabilities $\beta(0;0,0)$, the following processes for dynamic hyperpolarizabilities have been considered: EOPE $\beta(-\omega;\omega,0)$ and DC-EFISHG $\gamma(-2\omega;\omega,\omega,0)$. The electric dipole moments, some significant calculated magnitudes of static first hyperpolarizabilities, dynamic second, and third-order hyperpolarizabilities are shown in Tables 1, 2, 3, and 4, respectively. It is seen from Table 1 that compound 1 has higher value of μ while its second and third-order NLO phenomena has been obtained to be worser than compound 2. Both compounds in Fig.1 have second and third-order NLO behavior with non-zero $\beta-V$ and $\langle\gamma\rangle$ (Tables 2, 3, and 4). It has been found that static $\beta-V$, dynamic $\beta-V$, and $\langle\gamma\rangle$ values in Tables 2, 3, and 4 have an obvious enhancement in the order $1 < 2$. Compound 2 has higher quadratic ($\beta-V$) and cubic ($\langle\gamma\rangle$) hyperpolarizabilities, and hence has better second and third-order optical nonlinearities than compound 1. In particular, carotenoids and porphyrins like biological structures studied here have been shown in the literature [18, 20, 21] to have second hyperpolarizabilities with large magnitudes. Therefore, the examined molecules tend to give rise to strong third-order hyperpolarizabilities (see Table 4), which can be used to study pigment–pigment and pigment–protein interactions in photosynthetic complexes with different compositions of pigments and altered protein structures.

Conclusions

In this paper, the electric dipole moments, static first hyperpolarizability, dynamic first and second hyperpolarizability values of 1 and 2 have been calculated by TDHF method with

Table 3 Some selected components of the frequency-dependent $\beta(-\omega;\omega,0)$ and $\beta-V$ ($\times 10^{-30}$ esu) values at ω =0.04282 a.u. for 1–2

Compound	β_{xxx}	β_{yyy}	β_{zzz}	β_x	β_y	β_z	$\beta-V$
1	3.057	9.555	14.426	1.441	−0.066	6.480	6.638
2	−4.619	0.016	0.001	−13.575	−1.301	0.000	13.637

Table 4 Some selected components of the frequency-dependent $\gamma(-2\omega;\omega,\omega,0)$ and absolute values of $\langle\gamma\rangle(-2\omega;\omega,\omega,0)$ ($\times 10^{-37}$ esu) at ω =0.04282 a.u. for 1–2

Compound	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}	γ_{xxyy}	γ_{xxzz}	γ_{yyzz}	$\langle\gamma\rangle$
1	−187.622	120.268	12,962.452	−19.129	−129.379	−161.606	1758.368
2	53,906.651	−11.012	−0.697	−247.620	−0.016	1.966	10,706.677

6-31G(*d*) polarized basis set. The ab-initio calculated non-zero μ values of both compounds show that 1 and 2 might have microscopic first and second hyperpolarizabilities with non-zero values obtained by the numerical second- and third-derivatives, respectively, of the electric dipole moments according to the applied field strength. It is seen from the connection between the electric dipole moments and the first and second hyperpolarizabilities of the investigated compounds that crocin with less dipole moment as compared to chlorophyll *a* is characterized by higher calculated values of $\beta - V$ and $\langle\gamma\rangle$. Our theoretical results clearly show that the values of the second-and third-order hyperpolarizabilities make these materials interesting for future NLO applications.

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