

Quantum calculations of NLO properties for a series of natural pigments extracted from spinach

A. MIGALSKA-ZALAS^a, E. JANKOWSKA-SAHRAOUI^{b*}, K. BOUCHOUIT^c

^a*Institute of Physics, J. Dlugosz Academy of Czestochowa, PL-42217, Aleja Armii Krajowej 13/15, Czestochowa, Poland*

^b*Institut de Mathématiques Appliquées, Université Catholique de l'Ouest, 44 rue Rabelais, B.P.10808, 49008 Angers, France*

^c*Département de Chimie, Faculté des Sciences, Université de Jijel, Algeria*

Quantum chemical simulations of absorption spectra and second order molecular hyperpolarizability for a series of natural pigments extracted from spinach using a semi-empirical approach were performed. The studied molecules possess functional: hydroxyl, methyl and oxygen groups, which significantly modify the physical properties of particles. Analysis of the contribution of particular molecular group on the nonlinear optical properties is done. The theoretical calculation show that the second-order hyperpolarizabilities γ depends from the wavelength of incident electromagnetic radiation. The presence of functional groups attached to the back side hexagonal rings causes the substantial changes of both absorption spectra as well as nonlinear transmission and nonlinear optical coefficients. A big enhancement of the molecular cubic hyperpolarizability in these systems for several wavelength of incident light beam was shown. A comparison between the performed theoretical simulations and experimental results shows the possibility of using the proposed methods for prediction the contribution of individual parts of the molecules on the nonlinear optical coefficients.

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1. Introduction

Investigation of nonlinear optical materials has been the subject of extensive theoretical and experimental interest because of their potential applications in the development of photonic device such as optical data storage, optical communication, and optical limiting [1-4]. There are many research have been devoted to understanding the nature of the NLO phenomenon on organic compounds [5,6]. Most of the study now concentrates on organic materials with $\pi \rightarrow \pi^*$ electronic transitions because they are superior with regard to the molecular hyperpolarizabilities. In particular, the organic charge transfers containing a donor and an acceptor have been widely investigated as a representative of highly efficient NLO materials due to the strong charge transfer (CT) transitions [7-9]. The molecular structures of carotenoids present donor- π -acceptor forms, which are very promising candidates for applications in optoelectronics, quantum electronic optical communications, and also in the field of molecular engineering of functional materials [10-12]. Carotenoids are a group of natural pigments occurring in fruits and vegetables flavoring their colours from yellow to red. In human health, their importance is related to their actions as provitamin A, antioxidants, cell differentiation and proliferation regulators, cell-cell communication stimulators, immune function and carcinogen metabolism modulators, as well as blue light filters. There are many studies showing strong correlations between carotenoids intake both with the improvement of the immune system

and with the reduction of the risk of some degenerative diseases such as cancer, cardiovascular diseases, cataract and macular degeneration [13,14]. Functionalized carotenoids compounds with functional: hydroxyl, methyl and oxygen groups are materials interesting for the study of the linear, nonlinear optical properties and electronic transfer processes. The studied molecules (Fig. 1.) possess both electron donating and electron accepting character through the functional groups. Connecting donor and acceptor moieties with a conjugated bridge is a well established strategy to obtain molecules with high values of nonlinear hyperpolarizability.

The main goal in this distribution is to deduce the physical origin of the nonlinear optical phenomena of the investigated molecules and the point out the influence of the functionalization of these molecular structures on the improvement of their NLO properties. This work reported theoretical calculations of UV spectra and second order frequency-dependent molecular hyperpolarizability of the carotenoids in order to propose a NLO study of these molecules on a molecular scale. The proposed theoretical approach rely on geometry optimisation and corresponding quantum chemical calculations based on semi-empirical PM3 method within a framework of the restricted Hartree-Fock approach. For the theoretical calculation we use semi-empirical PM3 method as this is powerful and appropriate tool for simulation of the excited states properties such as oscillator strengths and excitation energies of large molecular. Moreover is very appropriate method to calculate linear and nonlinear optical properties of large molecules. In order to deduced the values of

third-order nonlinear optical susceptibility $\chi^{<3>}$ degenerate four wave mixing efficiency (at $\lambda = 532$ nm) as a function of the intensity of the wave pumps and nonlinear transmission for all compounds were done. Comparison of theoretical results with experimental data may give important information concerning the origin of the observed spectra and nonlinear optical properties. This comparison highlights the difference between theoretical values of the hyperpolarizability with the molecule in gas phase environment and experimental values obtained in polar solvents. The quantum chemical calculations give important information relating to the changes of propriety of material using the suitable substituent group.

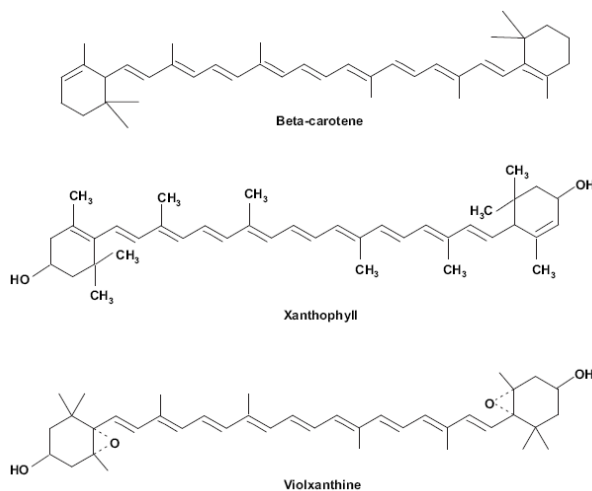


Fig. 1. Chemical structures of the investigated pigments.

2. Theoretical simulation

For theoretical simulations of absorption spectrum the three kind of different chromophores: Beta-Carotene, Violaxanthin, Xanthophyll (Fig. 1.) were considered. Initially geometry optimization (searching of the total energy minimum) for the molecule was performed. The MM⁷ molecular force field method was used for total energy minimization and for building of the molecular optimized geometry [15,16]. All quantum chemical calculations were performed by semi-empirical PM3 [17,18] method within a framework of the restricted Hartree-Fock approach and convergence limit up to 10^{-6} eV after 500 iterations was achieved. The calculations mixes all single determinant wavefunctions that can be obtained from the ground state by exciting electrons from a subset of the occupied orbitals to a subset of the unoccupied orbitals. The subsets are specified by an energy criterion associated with the energy difference between the occupied orbital and the unoccupied orbital. The electronic spectra were calculated by the configuration interaction (CI) method with the maximum excitation energy up to 9 eV. Local perturbation were considered only within a framework of the isolated molecule in vacuum. The influence of the intermolecular

electron vibration interactions is not taken into account. Therefore deviations from the experimental data will give information concerning the observed intermolecular interactions.

The intensity of absorption was expressed by the formula [19].

$$\varepsilon_{x,y,z} = \omega \sum_{j=1}^N \left| \mu_j^{(x,y,z)} \right|^2 \exp \left(- \left(\frac{E - E_j}{H} \right)^2 \right) \quad (1)$$

Where j - number of transition from ground state, $E_j = \hbar \omega_j$ - transition energy, $\mu_j^{(x,y,z)}$ - transition dipole component. The empirical parameter H was chosen at reasonable value of 0,5 eV, what gives the best agreement in lineshape of calculated spectra comparing to experimental results.

The PM3 semi-empirical method is used for the interpretation of ultraviolet spectral data since this technique is suitable to the calculation of excited state properties such as oscillator strengths and excitation energies. In this case it is possible to determine the hyperpolarizability via the sum-over-states formulation.

The total dipole moment induced by the electric field μ_{ind} is often written as a Taylor series expression in the electric field F . Here μ_0 is the permanent dipole moment, α , is the linear polarizability, β and γ the suitable hyperpolarizability.

$$\mu_{ind} = \mu_0 + \alpha^T F + \frac{1}{2!} \beta^T F^2 + \frac{1}{3!} \gamma^T F^3 + \dots$$

where,

$$F = F_0 + F_\omega \cos \omega t \quad (2)$$

In this case the energy expression is a simply related to equation (2). The sum - over-states expression for γ comes from the fourth order term in expansion (3).

$$E = E_0 - \alpha^T F - \frac{1}{2!} \alpha^T F^2 - \frac{1}{3!} \beta^T F^3 - \frac{1}{4!} \gamma^T F^4 \dots \quad (3)$$

When the interacting beam are at the the same frequency how it is in the case of DFWM experiment the expression described the values of second order hyperpolarizability simplified to the equation (4) and may be expressed in terms of the different energy levels from g to n , of the molecule.

$$\gamma_{ijkl}(-\omega, \omega, \omega, \omega) = K \sum_{g=1}^n \frac{\left| \mu_i^{(g)} \mu_j^{(g)} \left[M_k^{(g)} - M_k^{(0)} \right] \left[M_l^{(g)} - M_l^{(0)} \right] \right|}{(E_g^2 - (2\hbar\omega)^2 + H)} \quad (4)$$

where $\mu_i^{(g)}, \mu_j^{(g)}$ are the transition dipole moment between the high occupied molecular orbital (HOMO) and the excited state, $\left| M_k^{(g)} - M_k^{(0)} \right|$ is the difference between the excited (configuration interaction (CI) level) state

dipole moment and ground state one, E_g is the transition energy from the ground to excited state, $\hbar\omega$ is the energy of a incident laser photon, H determines the line shape broadening, n is a number of excited state. Indices: $i, j, k, l = x, y, z$ are defined as laboratory Coordinate Cartesian system. In a present work we calculated only γ_{xxxx} , where x direction corresponds to the maximal permanent dipole moment. The calculated values of the nonlinear optical hyperpolarizabilities are presented in the Table 3.

3. Experimental measurements

Third order nonlinear optical susceptibilities of Beta-Carotene, Violaxanthin and Xanthophyll solutions were measured by the standard backward degenerate four wave mixing (DFWM) method using Nd:YAG laser working at 532 nm with pulses duration of 30 ps and 1 Hz repetition rate. In DFWM geometry, two strong, equal intensity, counter-propagating pump beams and a weak probe beam were temporally and spatially overlapped in the sample. A phase-conjugated signal generated from these three laser beams of the same frequency was collected at a reverse direction of the probe beam. This signal was measured by photomultiplier tube and fed to a digital storage oscilloscope. A part of the input laser beam was split off and measured by a sensitive photodiode in order to monitor the input laser energies as well as their related fluctuations. The studied compounds were dissolved in dichloroethane and contained in a 1 mm thick cuvette. The solvent produced signal under the experimental conditions. Third order nonlinear optical susceptibility of dichloroethane was estimated to be $\chi^{<3>} = 0.13 \cdot 10^{-20} [m^2/V^2]$. We used carbon disulfide (CS_2) as reference material to calibrate DFWM measurements. Third order nonlinear optical susceptibility of CS_2 was estimated to be $\chi^{<3>} = 1.94 \cdot 10^{-20} [m^2/V^2]$. DFWM may include the orientational and dynamic resonant nonlinearity contributions, depending on the experimental conditions. This means that the DFWM technique may be used to measure different contributions, including electronic, orientation and thermal effects.

In general, the third order nonlinear optical susceptibility ($\chi^{<3>}$) is considered to be a complex quantity $\chi^{<3>} = \chi_R^{<3>} + i\chi_I^{<3>}$ where the real part, ($\chi_R^{<3>}$), is related to the nonlinear refractive index changes, which can be extracted from DFWM measurements. The imaginary part, ($\chi_I^{<3>}$), is related to the two-photon absorption coefficient (β) calculated from nonlinear transmission (NLT) measurement.

The nonlinear transmission was calculated using the following expression:

$$T = \frac{I_T(L)}{I_1(0)} = \frac{\alpha \exp(-\alpha L)}{\alpha + \beta I_1(1 - \exp(-\alpha L))} \quad (5)$$

where α is the linear absorption coefficient; $\beta = 24 \frac{\omega \pi^2}{n^2 c^2} \chi_I^{<3>}$, the two photon absorption (TPA) coefficient; L , the thickness of the sample; I_1 and I_T , respectively the incident and transmitted intensities.

Fig. 5. displays the nonlinear transmission behaviour of beta-carotene and violaxanthin. All values of the linear absorption coefficient (α) of the investigated compounds, which were deduced from $T = \exp(-\alpha L)$, are reported in Table 1.

The measured and calculated third-order susceptibility for the investigated molecules were presented in the Table 2 and Table 3. More details concerning the measurements of third-order susceptibility and degenerate four wave mixing technique at fundamental wavelength of 532 nm you can find in Ref [20].

4. Results and discussion

The calculated absorption spectrum for the investigated molecules are presented in Fig. 2. These spectra present the typical absorption band at 200-500 nm which is associated to $\pi \rightarrow \pi^*$ electronic transitions of the carotenoids chromophores from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).

The position of the strongest peaks of the calculated spectra using PM3 semi empirical molecular orbital model are blue shifted with respect to experimental peak position (Fig. 3.). For longer wavelength we have the larger divergence what is connected with vibration system which plays an important role in the observed differences.

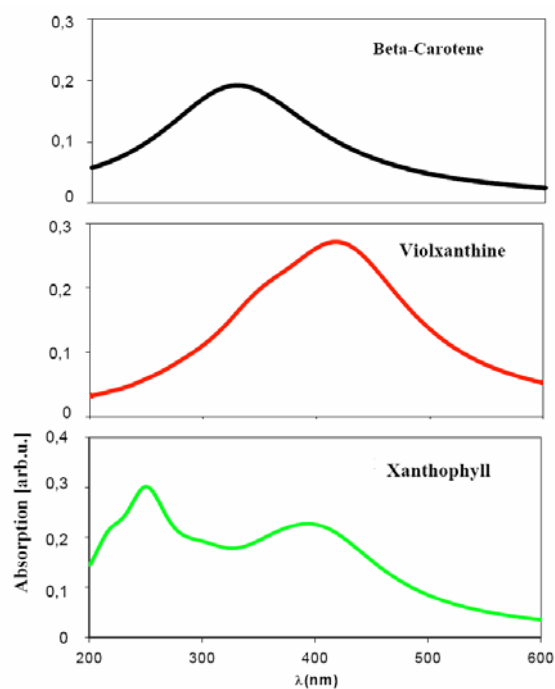


Fig. 2. Calculated absorption spectra of studied carotenoids.

The shift of the absorption spectra may be related with the specific geometry of the carotenoids. The second reason of the difference between the theoretical and experimental results of absorption spectra could be a quantum chemical calculations without taking into account interaction between molecule and solvent polarity [21]. The presence of methylic and hydroxylic groups changes the electronic properties of the carotenoids.

The calculated HOMO and LUMO gaps as well as total dipole moments are presented in the Table 2. The latter play important role in the NLO properties. One can see that for the Beta-Carotene HOMO-LUMO energy splitting gap is largest than for the remaining samples. A very important parameter is a difference between the ground and excited dipole moments. We can see that the kind of bonds in this molecule increase HOMO-LUMO energy splitting gap but decrease the ground state dipole moment comparing to the other samples what enlarges NLO coefficient. Presence of functional OH group in Violaxanthin and Xanthophyll increase the polarity and the static dipole moment. A large dipole moment and HOMO-LUMO difference leads to a reduction of second-order hyperpolarizabilities in these systems what it results directly from equation 4.

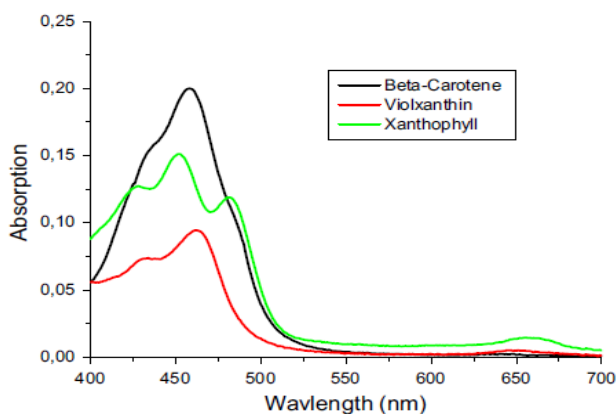


Fig. 3. Typical experimental absorption spectra of the examined molecules.

The imaginary part, $(\chi_i^{<3>})$, is related to the two-photon absorption coefficient (β) calculated from nonlinear transmission (NLT) measurement.

Fig. 4. displays the nonlinear transmission behaviour of Beta-Carotene and Violaxanthin. It means that the nonlinear transmission decrease with an increase of the incident intensity. Therefore, these samples reveal the

nonlinear absorption. The values of two photon absorption (TPA) coefficient (β), which can be related directly to the imaginary parts of third order nonlinear optical susceptibility ($\chi_i^{<3>}$), were extracted from dependencies of experimental data and equation (5). The obtained values of TPA coefficient (β) for Beta-Carotene and Violaxanthin dissolved in dichloroethane are presented in Table 1.

In the case of Xanthophyll we obtained a nonlinear transmission curve constant with the incident intensity and the transmission value was lower than unity (see Figure 4). This allowed to consider only a one-photon contribution to the absorption and to conclude that the third order nonlinear optical susceptibility is a real parameter at the excitation wavelength of 532 nm, ($\chi_i^{<3>} = 0$). All values of the linear absorption coefficient (α) of the investigated compounds, which were deduced from $T = \exp(-\alpha L)$, are reported in Table 1.

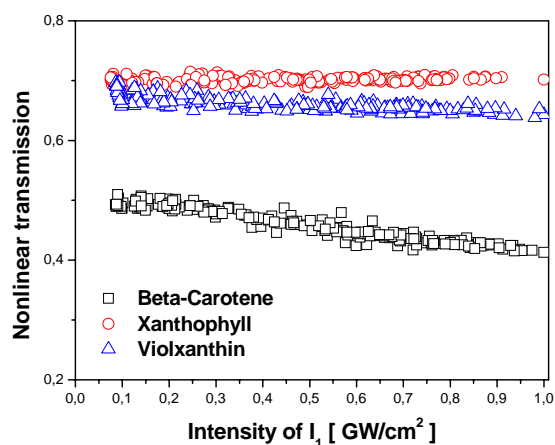


Fig. 4. Nonlinear transmission of Beta-Carotene, Violaxanthin and Xanthophyll as a function of input pump intensity.

Figs: 5a, 5b, 5c. presents the calculated molecular orbital wavefunctions corresponding to the HOMO and LUMO orbitals. HOMO-LUMO maps indicate higher probability of finding an electron in the areas of bonds and free electron pairs.

Table 1. The values of linear absorption coefficient (α), two-photon absorption coefficient (β), the imaginary part of third order nonlinear optical susceptibility ($\chi^{<3>}$) and the absolute value of third order nonlinear optical susceptibility ($|\chi^{<3>}|$) of Beta-Carotene, Violaxanthin and Xanthophylls dissolved in dichloroethane at a measurement wavelength of 532 nm, respectively.

Molecule	α (cm^{-1})	β (cm/GW)	$\text{Im } \chi^{<3>}$ (m^2/V^2)	$ \chi^{<3>} $ (m^2/V^2)
Beta-Carotene	6,63	8,68	$2.65 \cdot 10^{-20}$	$2,87 \cdot 10^{-20}$
Violxanthine	3,94	1,87	$0.57 \cdot 10^{-20}$	$0.63 \cdot 10^{-20}$
Xanthophyll	3,59	≈ 0	-	$0,35 \cdot 10^{-20}$

We should point out the fragments contributing to the obtained results and we present only the largest contributions connected with influence the MO wave functions. In this case main role belongs to the fragments that are placed on back side of the molecule containing unsaturated hexagons rings with the functional groups. The presented contours show how the change of the chemical bonds may change the total molecular charge density contributions. A high charge delocalization is observed for all compounds what is typical for a molecules with donor and acceptor groups. In such molecules charge jump over one part of molecule to the other, what causes a large asymmetries of molecule and large change of dipolar moment in basic and excited state. This asymmetry in the ground and excited state topology plays important role in the observed nonlinear optical properties. Therefore, the

backside groups of the molecules play a central role in determining of the electron charge density non-centrosymmetry that influences on the nonlinear optical properties.

We present the measured third-order susceptibility and the calculated hyperpolarizabilities for the investigated molecules in the Table 1 and Table 3. The calculated values of second order hyperparizabilities at the incident light wavelengths 532 nm obtained for the investigated pigments are comparable with the nonlinear coefficients obtained for similar molecules presented in Ref [22]. We can see that the adjunction of a functional hydroxyl group in the Beta-Caroten lead to the substantial increase of the cubic hyperpolarisability γ . It can be explained by longer extent of molecule favouring electron delocalization.

Table 2. Values of calculated properties of carotenoids.

Molecule	Totale Dipole moment (D)	HOMO (EV)	LUMO (ev)	Optical gap (eV)
Beta-Carotene	1,24	-7,77	-0,94	6,83
Violxanthine	8,79	-7,12	-0.72	6,40
Xanthophyll	9,05	-6,46	-1,39	5.07
CS ₂	-	-	-	-

From the other side the remaining molecules are more stabilised owing to pronounced larger dipole moments presented in the Table 2

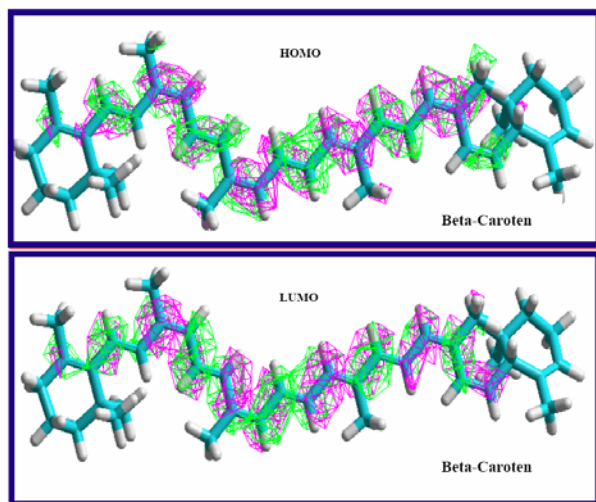


Fig. 5a. Electrostatic potential distribution HOMO and LUMO for Beta-Caroten.

The calculated hyperpolarizabilities of the studied pigments decrease in the order of Beta-Carotene > Violaxanthin > Xanthophyll what well correlates with experimental results [23].

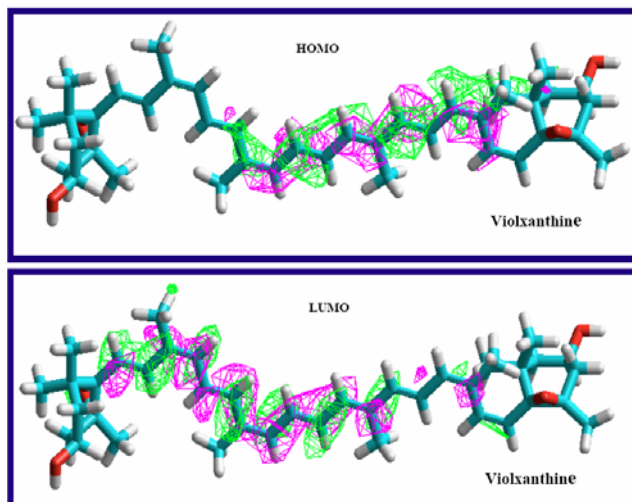


Fig. 5b. Electrostatic potential distribution HOMO and LUMO for Violaxanthin.

Fig. 6. presents dispersion of the molecular second order hyperpolarizabilities for the investigated molecules. The data were obtained using formula (2). Frequency-dependent hyperpolarizabilities to possibly used in investigations of propriety of particles different materials change with change of wavelength incident light what is very important for nonlinear optics and molecular engineering. From the Fig. 6. we can see a drastic increase

of nonlinear coefficient γ for Beta-Carotene and Violaxanthin for several wavelength of incident light beam. The maximum values of the coefficient γ and wavelengths for which they are achieved are summarized in Table 3.

From Fig. 6. and Table 3 it can be noticed that the absolute values of third order nonlinear optical coefficient of Beta-Carotene and Violaxanthin is about two times bigger than for Xanthophyll. Such behaviour is caused by highly conjugated system and occurrence of hydrocarbon lacking functional groups in these compounds. The molecular structure of Beta-Carotene and Violaxanthin does not consist of oxygen atoms. In comparison with the mentioned pigments Xanthophyll is oxidized derivatives of carotenes and it contains hydroxyl groups. Contrary to the carotenes, hydroxyl groups substitute some hydrogen atoms and/or oxygen atoms substitute some pairs of hydrogen atoms what substantially reduce the nonlinear optical properties.

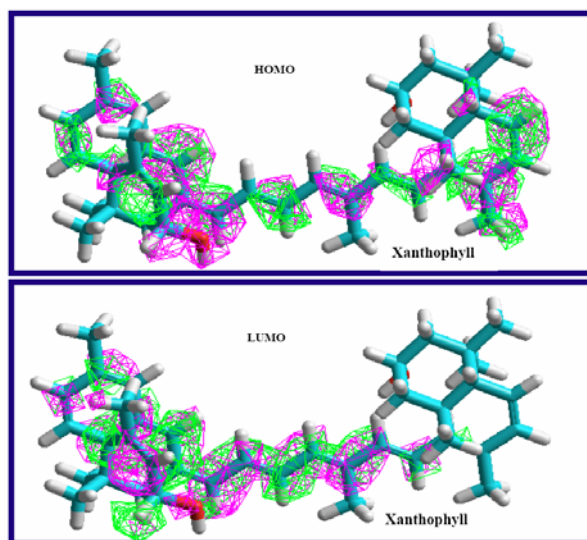


Fig. 5c. Electrostatic potential distribution HOMO and LUMO for Xanthophyll.

The carotenoids are radicals of different natures, one donor and one acceptor and have a large third-order nonlinearity since the radicals add their effects, thus intensify the asymmetric distortion of the conjugated system. Further the electronic properties of this type of molecule exhibit a unusual property, the intramolecular [24] charge transfer between the two radicals.

The nonlinear optical coefficients measured by DFWM are very sensitive to the local field correction and any incompatibilities can result also is almost entirely due to the way this correction is performed what can be also reason of any incompatibility.

Table 3. Values of calculated and measured nonlinear optical properties of third order. $\chi^{(3)}$, Susceptibilities of third order, γ_{xxxx} hyperpolarizabilities of second order,

Compounds	$\chi^{(3)}$ [m ² /V ²] [23]	γ_{xxxx} (esu) Calculated at $\lambda = 532$ nm	γ_{xxxx} (cal.) maximal and λ for which was obtained	
			γ_{xxxx} (esu)	λ (nm)
Beta-Carotene	$2,87 \times 10^{-20}$	$1,54 \times 10^{-36}$	1.15×10^{-32}	831
Violxanthine	$0,63 \times 10^{-20}$	1.26×10^{-36}	2.40×10^{-32}	946
Xanthophyll	$0,35 \times 10^{-20}$	6.77×10^{-37}	1.60×10^{-34}	417
CS ₂	$3,36 \times 10^{-35}$	$3,95 \times 10^{-35}$	-	-

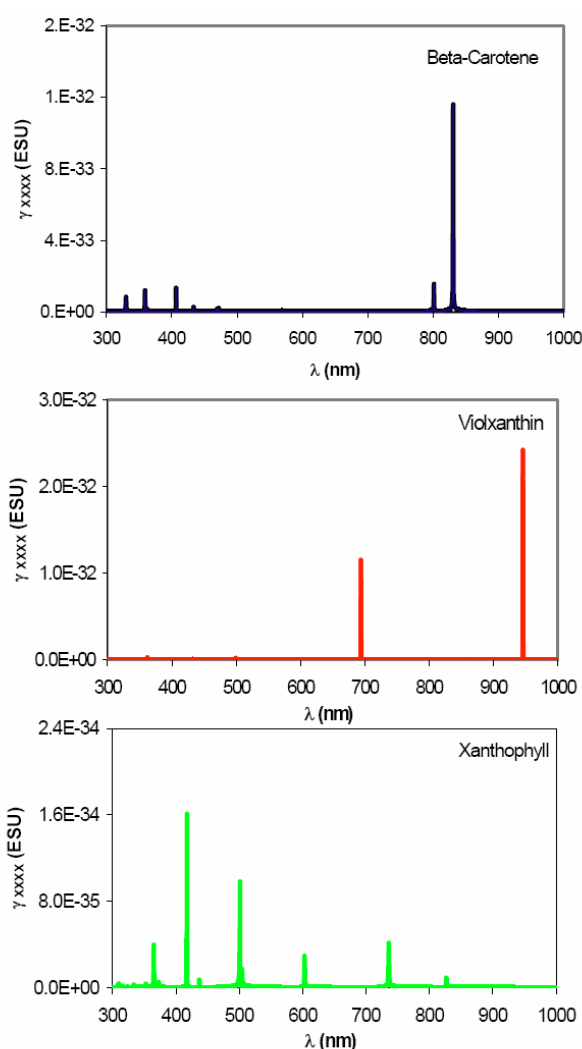


Fig. 6. Dispersion of the molecular third order polarizabilities $\gamma(-\omega, \omega, \omega, \omega)$ for the investigated molecules.

The reason of this could be also simply attributed to the possible errors in quantum – chemical methods, but we cannot rule out a strong influence of the solvent effect. Taking under attention the different mechanism of formation of nonlinearity in experiment and introduced in calculations we can compare the only trend of changes of non-linear coefficient collected in Table 3. We can say that we have good correlations between the theoretical calculations and experimental data for all compounds.

5. Conclusions

We have investigated contribution of the different functional groups in carotenoids to the output of nonlinear coefficient as well as UV spectra. The theoretically calculated absorption spectral positions are blue shifted in comparison to the experimental spectra for all compounds. Comparison of measured and calculated by quantum chemical PM3 method results manifests good agreement with the experimental data. Different moieties causes the substantial changes of nonlinear transmission and nonlinear optical coefficients. One found that the hydrocarbon lacking functional groups in highly conjugated Beta-Carotene stimulates increasing of NLO coefficient. The presented calculations showed how values of nonlinear optical coefficient changes in dependence of wavelength. The results of quantum chemical calculations can provide the basis for finding of compliance of the calculated and experimental electronic properties in such kinds molecules. The study of nonlinear effects of investigated pigments is interesting for its applicative potential allows a thorough characterization of new materials with strong NLO properties and materials for data storage. The data thus obtained provide valuable insight into the origin of the hyperpolarizability and help to synthesize molecules with optimal properties. As a matter of fact, the knowledge of such phenomena produced in excited media using ultra fast laser light. One we can conclude that characterizations and studies of natural pigments with ultra fast laser light could be a key element for discovering new NLO properties performances of optoelectronics devices.

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*Corresponding author: emiliasahraoui@yahoo.fr