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Theoretical calculation of NLO properties of some selected σ -acetylide complexes

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The theoretical quantum chemical calculations of UV spectra and second order frequency-dependent molecular hyperpolarizability of σ -acetylide complexes, in order to propose a NLO study of these complexes on a molecular scale, was performed. For the numerical analysis, the electronic states obtained in the semi-empirical ZINDO/1 approximation within a framework of the Restricted Hartree-Fock approach with the singly excited configuration interaction method are used. Second - order hyperpolarizability γ of the organometallics has been calculated for the degenerate four wave mixing at several incident frequencies using the sum-over-state (SOS) method. The quantum chemical calculations give important informations concerning the origin of the observed spectra and information for advisable changes of the chemical content using appropriate ligands. Moreover, the information about nonlinear optical properties of the investigated molecules is crucial in order to increase the nonlinear optical response of the compounds under consideration and also for their functionalizations. Good agreement between the theoretically calculated and experimentally measured spectra was observed. Analysis of the theoretical spectra shows a substantial sensitivity to the backside groups. The theoretical calculations show that the second – order hyperpolarizabilities γ strongly depends on the wavelength of incident electromagnetic radiation. We show a big enhancement of the molecular cubic hyperpolarizability in these systems for several wavelength of incident light beam. Comparison of theoretical results with the experimental data is presented.

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1. Introduction

Carbon-rich organometallics containing fixed π–conjugated chains is an important class of organometallics nanocomposites for the investigation of electron-transfer processes, the construction of molecular devices and novel materials for non-linear optics (NLO) [1-3]. Among them, σ-acetylide complexes represent one of the widely investigated classes of second-order NLO metal complex.

The interest of the organometallic complexes in NLO comes from their particular electronic capacities in term of charge transfer [4-6]. Indeed, their optical spectra often present intense transitions in visible bringing into play the metal-ligand charge transfer (MLCT) or conversely. In particular, the acetylide organometallic complexes having a linear structure of type M-C≡C-R generate a strong coupling between metal and π-conjugated fragment which lead consequently to strong optical non-linearities [7,8]. This work is located in this specific field of research. Theoretical and experimental studies on these complexes showed that the strong hyperpolarisability of the second and third order characterizing the nonlinear optical efficiency of the molecule depends on the length of the π-conjugated grafted fragment and the force of the donor groups (metal) and acceptor. In organometalics, the metal-ligand bondings look forward to point large molecular hyperpolarizabillity because of the transfer of the electrons between the metal and the conjugated system.

Relationships between the chemical structure and the second - order hyperpolarizabillity γ of molecule are very important to enlarge the nonlinear values. The strategies to improve the second – order hyperpolarizability of a molecule, and consequently the third – order susceptibility $\chi^{(3)}$ of a substance, are not as well developed as in second - order nonlinear optics. There are two main approaches can be discriminate: optimization of small chromophores by substituting strong and electron donor acceptor groups [9] with molecular orbital's of the π-conjugated system and organomethallic complex with the overlaping of *d* atomic orbital's of ruthenium. These molecules have an overall fixed configuration, and the transition-metal interacts with the **π**-electrons of the carbon chain structure, leading to a more delocalized **π**-electron system.

The present study is a natural continuation of our previous work concerning the analysis of nonlinear optical properties of other families of alkynyl-ruthenium complexes [10-12]. In this paper, we present the theoretical quantum chemical calculation of UV spectra and second order frequency-dependent molecular hyperpolarizabillity a novel series of donor-acceptor ruthenium chromophores possessing the chemical formula presented in the Fig. 1. The performance of the UV-VIS spectra is necessary to have an idea about the further modifications of the materials. The quantum chemical calculations give important information concerning the origin of the observed spectra and information for desirable changes of the chemical content using the appropriate ligands. The extraction of the NLO parameters is the key for the optimisation of nonlinear optical response. Especial attention will be devoted to the delocalisation of π electrons along the molecular backbone influence of different ligands on the output of third order optical properties and a spectral shift of UV absorption. The synthetic methodologies employed for the preparation of the new ruthenium derivatives have been adapted from previously reported procedures in the reference [13-15].

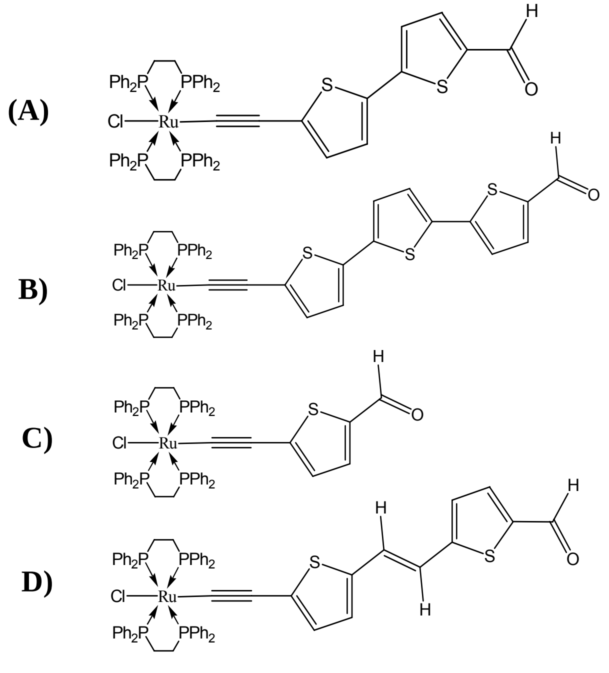


Fig. 1. Chemical structures of the studied compounds: A, B , C, D.

2. Theoretical simulation

For theoretical simulations of absorption spectrum and second-order molecular hyperpolarizability the four different types based on different chromophores (molecules indicated by: A, B, C, D – Fig. 1.) were considered.

Geometry optimization for the molecule was performed using the MM$^+$ molecular force field method for total energy minimization and for building of the molecular optimized geometry [16,17]. All quantum chemical calculations were performed by semi-empirical ZINDO/1 method with the singly exited configuration within a framework of the restricted Hartree-Fock approach. The ZINDO/1 method was optimized as a universal semi-empirical method for calculating energy states in molecules containing transition metals (3d and 4d).

The electronic spectra were calculated by the configuration interaction (CI) method with the maximum excitation energy up to 9 eV. 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 intra-molecular and intermolecular interactions. The intensity of absorption was expressed by the formula:

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

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 lineshipe of calculated spectra comparing to experimental results.

The ZINDO/1 semi-empirical method is used for the interpretation of ultraviolet spectral data since this technique is suitable to the calculation of exited state properties such as oscillator strengths and excitation energies [18,19]. In this case it is possible to determine the hyperpolarizability via the sum –over-states formulation.

The values of second order hyperpolarizabillity can be expressed in terms of the different molecular energy levels from g to n, of the molecule.

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

where: $\mu_i^{(g)}, \mu_j^{(g)}$ - are the transition dipole moment between the high occupied molecular orbital (HOMO) and the exited state; $\left|M_k^{(g)} - M_k^{(0)}\right|$ - difference between the excited (configuration interaction (CI) level) state dipole moment and ground state dipole moment, E_g - transition energy from the ground to exited state; $\hbar\omega$ - is the energy of a incident laser photon; H – determines the line shape broadening (0,12eV); n – a number of exited state. Index i, j, k, l = x, y, z are defined as laboratory Coordinate Cartesian system where x – axis corresponds to the longest axes of the molecule.

In a present work we calculated only γ_{xxxx}, because the maximal output of nonlinear signal were observed usually for the diagonal tensor component, where the x- direction corresponds to polarizations direction of the photo inducing beam. The calculated values of the nonlinear optical hyperpolarizabilities are presented in Fig. 4. and in Table 2.

3. Results and discussion

As a criterion of agreement of theoretical and experimental data the confrontation of experimental spectrum with calculated in frame of described model was used.

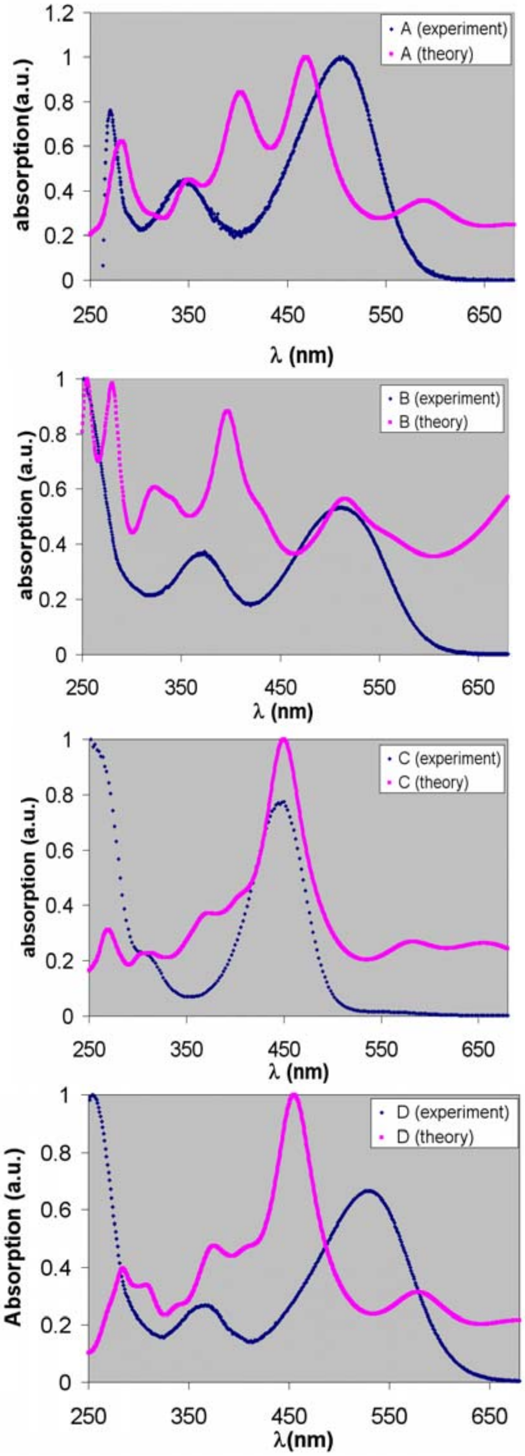


Fig.2. Comparison between calculated and experimental spectra for compounds A, B, C, D.

The comparison of calculated and measured UV-spectra of the selected molecules are presented in Fig. 2. The experimental UV spectra were performed in chloroform solutions at low concentration (~10^{-5} mol/l). From the measured and calculated spectrum some interesting characteristic could be deduced such as bands responsible for charge transfer can be observed. The electronic spectra contain a metal–to–alkynyl charge transfer band as the dominant low energy transition. In all cases, metal-to-phosphorus charge transfer also plays a significant role. The bands in the range of 330-460 nm were assigned to thiophene – based π-π^* transitions and localized over the whole complex. Also the bands 270 – 320 can be observed which areas well responsible for π-π^* transitions due to C=O and C=C groups. The intense band at 310 nm is due to chloro- metal charge transfer.

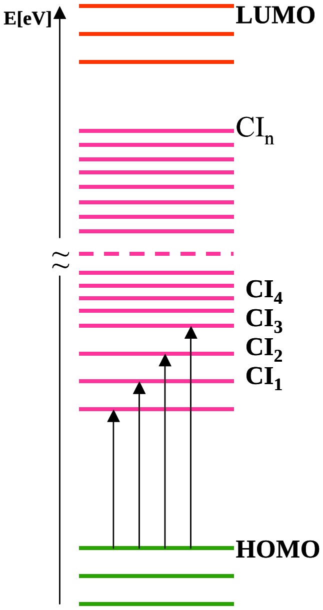
The calculated transition energies are generally in good agreement with the experimental results, differences being typically < 30 nm for compounds A, B, C. For the molecule D we have larger divergence. The presented in the Fig. 3. data unambiguously show that intramolecular interactions are dominant in the observed spectra.

Generally the better agreement is achieved for the molecule with lower state dipole moments (A, C), which indicates that this methods is appropriate for the more covalence compounds. The position of the three strongest peaks of the measured spectra is shifted to the region of larger wavelengths with respect to the calculated spectra. Generally for longer wavelength we have larger divergence what is connected with the right side of molecule (chlorium) which plays an important role in the vibration system. The second reason of disagreement 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 [20] because the absorption spectra of organic molecules in liquid solutions are known to be depend on the local electric fields generated by the surrounding polar molecules of solvent. From Fig. 3 one can conclude that for the molecule D the vibration and inter-molecular chromophore - solvent contributions can be very important [20]. In proposed theoretical simulation only electronic system was taken into account.

In Table 1 we present the calculated HOMO-LUMO energy gaps as well as parameters of the Configuration Interaction (CI) states and experimental energy gaps. It is clearly seen that the theoretically predicted HOMO-LUMO energy gap are relatively larger than the experimental energetic gap. From the energetic levels diagram (Scheme 1.) we can see a different energy level distribution CI_1-Cin, situated within the forbiden enegry gap what lead to the smaller HOMO-CI_1 energy gap. HOMO-CI_1 represent the transition of electron from the HOMO level to the first excited level CI_1 (CI_1correspond to the first peak in absorption spectrum) what correlate well with the experimental results. The appearance of an additional number of trapping levels lead to the occurrence of the larger number of the delocalized states within the forbidden energy gap, wchich are responsible for the appearance of long lived excitons favoring the additional polarization (what lead to the increase of nonlinear optical properties).

Table 1. Comparison of theoretical results with experimental data: Total dipole moments, HOMO - the highest occupied molecular orbital, LUMO - the Lowest Unocupied Molecular Orbital, Eg – energy gap Eg -experimental energetic gap, HOMO - CI_1 energetic difference among the highest occupied orbital molecular and first excited molecular orbital.

Molecule	Total dipole moments (D)	HOMO (eV)	LUMO (eV)	Optical Gap (eV) LUMO-HOMO	Eg (eV) Exp.	HOMO-CI_1 (eV) (theoret.)
A	20.58	0.15	3.95	3.8	2.14	2.08
B	26.19	0.35	3.75	3.4	2.07	2.03
C	21.75	0.05	3.85	3.8	2.48	2.31
D	23.54	0.12	3.91	3.79	1.97	1.94



Scheme 1. Diagram of energetic levels for molecule in vacum:, CI_1-CIn - configurationally excited energetistic exciton levels (CI - Configuration Interaction) situation within the optique energy gap.

One the other hand, we have also calculated one electron energy eigenvalues highest occupied molecular orbital and lowest unoccupied molecular orbital contours showed in Fig. 3.

Overlap between the HOMO and the LUMO is a governing factor in many reactions. An example of Frontier Orbital theory is in predicting sites of electrophilic attack aiming to join of electrons on aromatic compounds. If we plot the HOMO as a contour map, the region of highest density (regardless of sign) is generally the site of electrophilic attack. This is generally the site of reaction. In this example, the HOMO is plotted one Å above the plane of the molecule. It shows the place of electrophilic attack at the ruthenium adjacent to the phosphorus atoms. This is also the experimentally observed space. Particularly we show that the non-centrosymmetry of the charge density could lead to a substantial enhancement of the total dipole moments as well of the corresponding transition dipole moments between the HOMO states and excited CI states.

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 containing the Ruthenium atom. The presented contours also show how the small change of the backside group chemical bonds may change the total molecular charge density contributions. The right back-side groups of the molecule plays a central role in determining the electron charge density non-centrosymmetry that determines the third-order nonlinear optical properties described by fourth rank polar tensor. A higher charge delocalization is observed for compound D and A possessing two thiophene rings (compound A) and double bonds C=C between thiophene rings (compound D) in the backside chemical group. Let's compare for example the large difference in charge density distribution in the HOMO and LUMO for compounds A and D with the excellent molecular hyperpolarizability γ obtained for the mentioned molecules. At the same time the joined back side group in the molecule B and C compensates the gradients of the charge density resulting in essential decrease of the nolinear optical coefficient (see Table 2.). Such investigations give a possibility to operate by the chemical bonds in desirable direction in order to achieve an enhanced of the optical susceptibilities of higher orders. These maps give imagine about possible ways to perform molecular engineering manipulation within the presented compounds.

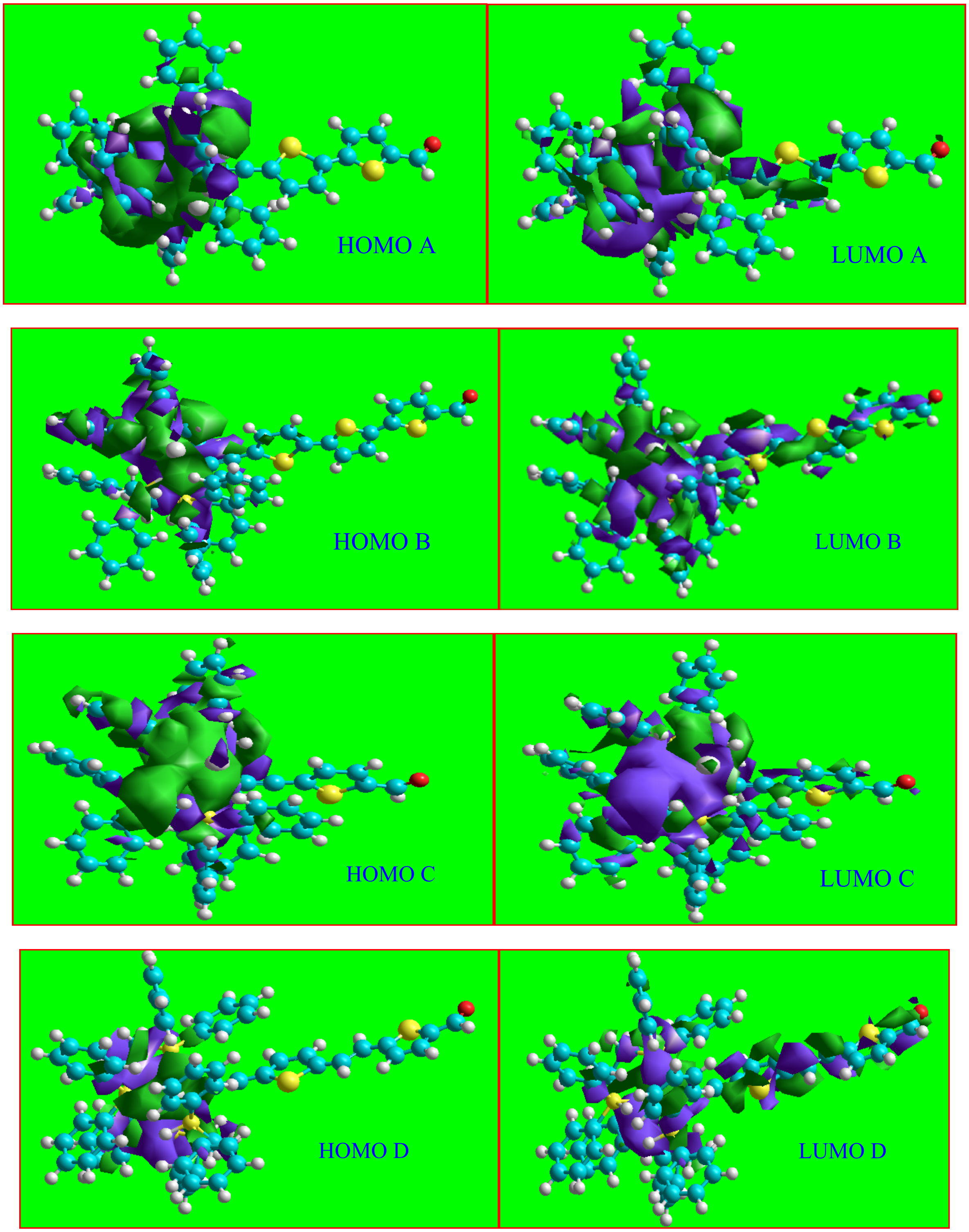


Fig. 3. Calculated HOMO and LUMO molecular orbital wave functions of the investigated compounds A, B, C, D.

Fig. 4. presents dispersion of the molecular second order hyperpolarizabilities for the investigated molecules. The data were obtained using formula 2. We can see that the results strongly depend on the incident light wavelengths. Frequency-dependent hyperpolarizabilities to possibly used in investigations of propriety of particles different materials change with change of wavelength incident light.

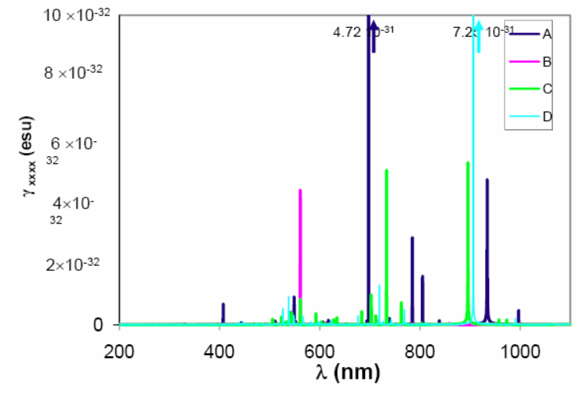


Fig. 4. Dispersion of the molecular third order polarizabilities $\gamma\,(-\omega, \omega, \omega, \omega)$ for the investigated molecules (A, B, C, D).

We can see that the adjunction of two thiophene rings to the end side group lead to a drastic increase of nonlinear coefficients for compounds A and D but in molecule C possessing three pentagon rings and for molecule with one thiophene ring causes a decrease of nonlinear answer. However the obtained second order hyperpolarizalilty for all the investigation in this work organomethallic compounds are very high compared to the other similar molecules or nitroanilines which are well-known from very good NLO properties presented in Ref [10,11,21,22]. This enhancement is due to the intramolecular donor-acceptor charge transfer.

It has been demonstrated that the existence of a high electronic delocalization on the π-conjugated chain extended on such type of systems lies at the origine of third order NLO phenomena. In fact, such properties arise mainly as a result of the overlaping of *d* atomic orbitals of ruthenium with molecular orbitals of the π-conjugated system, and this can be systematically modified by changing the π-conjugated system or the electronic content of ruthenium acetylide fragment. Theoretical quatum chemical simulations have shown that additional double bond between two thiophene ring in molecule D play an important role in the observed nonlinear optical dependencies. For compound D the additional C=C bond in the back side group enlarge the extent of electronic delocalizattion and facilitate the conjugation effect. A drastic increase of second order hyperpolarizability was observed for molecule D $\gamma_{xxxx} = 7{,}25 \times 10^{-31}$esu at the wavelength 907 nm and for molecule A possessing two thiophene ring $\gamma_{xxxx} = 4.72 \times 10^{-31}$esu at 698 nm (see Table 2.).

Table 2. Values of calculated and measured nonlinear optical properties.

MOLECULE	γ xxxx (ESU) MEASURED AT λ =532nm	γ xxxx (ESU) CALCULATED AT AROUND λ = 532nm	γ xxxx (CAL.) MAXIMAL AND λ FOR WHICH WAS OBTAINED $\lambda_{(MAX)}$(nm)	
Molecule A	3.5×10^{-30}	1.48×10^{-33}	4.72×10^{-31}	698
Molecule B	6.5×10^{-30}	1.2×10^{-34}	4.35×10^{-32}	562
Molecule C	1.7×10^{-30}	1.07×10^{-33}	5.24×10^{-32}	896
Molecule D	7.43×10^{-30}	9.12×10^{-33}	7.25×10^{-31}	907
CS_2	3.36×10^{-35}	3.95×10^{-35}	-	-

To check the above semi empirical results we compare our theoretical calculations with experiment. Deviations from the experimental and theoretical data give information concerning the observed intramolecular and intermolecular interactions. In this paper, we report the results obtained in the NLO characterization of a ruthenium chromophores incorporated in dichloromethane solvent. The third-order nonlinear optical susceptibilities of these solutions were measured by the degenerate four wave mixing (DFWM) technique at fundamental wavelength at 532 nm from a Nd:YAG laser with a pulse duration of 30 ps, at the repetition rate frequency of 1 Hz [23]. As you know two essential local effects contribute to nonlinearities in isotropic media submitted to such laser pulses: deformations of electronic cloud and molecular reorientation (translations, rotations and vibrations). The proposed theoretical approach is apply only for separate molecule without taking into account inter molecular interaction, molecule - molecule and molecule – solvent. 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 2. However the comparison of calculated and measured hyperpolarizabillity is very interesting and may provide some information about intremolecular interactions.

The values of calculated and measured nonlinear optical properties are presented in Table 2. From calculation it results that molecule D is the best candidate from among studied molecules for the nonlinear experimental investigation using laser wavelength close to 532 nm.The maximally achieved second order hyperpolarizability clouse to 532 nm was obtained for the mentioned compound and is equal γ_{xxxx} (cal.) = $9,12 \times 10^{-33}$ (esu) . The largest second-order hyperpolarizability γ_{xxxx} (exp) is measured also for compound D what is connected with the large electronic contribution to the observed results and it is peaceable with theoretical simulations. The good coincidence between theoretical and experimental data was obtained for the remaining compounds except molecule B. We can expect that for this molecule the inter and intra molecular electron vibration interactions plays a key role in the observed nonlinearities. The experimental results and theoretical ones suggest that better non-linear optical proprieties possess the compounds with two thiophen rings added in back side groups. Both theoretical and experimental studies have demonstrated that the strong hyperpolarizability of second order depends on the length of the π-conjugated chain and also on the strength of the donor and acceptor fragments. Moreover, it has been observed that the non linear response of the second order is rising due to the multiple metal-carbon bonds present in this type of complexes. It is well known that the greatest problem associated with non-linear optical compounds is connected not only with ideal molecules but also with the incorporation of these molecules to form ideal macroscopic samples for non-linear optics. So the preparation of the samples play a key role in giving non-linear optical properties to the samples, and this could be the reason of any disagreement between experimental and theoretical data. The reason is also simply attributed to the possible errors in quantum –chemical methods, but we cannot rule out a strong influence of the solvent effect.

3. Conclusions

We have theoretically investigated contribution of the backside group to the output of the nonlinear coefficient as well as a UV spectra for a new series of σ -acetylide complexes. The theoretical results for the molecule agree roughly with experimental data taking into consideration, of course a dispersion of the absorption fundamental edge caused by the intermolecular interactions. We have shown that the right side chemical radicals play essential role in the observed nonlinearities. We have found that the two tiophen rings in molecule A and D stimulates increasing NLO coefficient. Theoretical and experimental studies of σ-acetylide complexes have shown that the hyperpolarizability (γ) for all the investigation molecules depends on the strength of the donor and acceptor groups' extent on the π-conjugated system. We have found that the reason of any disagreement between the theoretical and experimental results is due to vibration and intermolecular contributions on the optical properties. The data thus obtained provide valuable insight into the origin of the hyperpolarizabillity and help to synthesize molecules with optimal properties. All investigations show that the materials under considerations are promising ones for the nonlinear optics molecular engineering.

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