

Large third-order nonlinear optical properties of alkynyl ruthenium chromophore thin films using third harmonic generation

JEROME LUC, JEAN-LUC FILLAUT^a, JACEK NIZIOL^b, BOUCHTA SAHRAOUI

*Université d'Angers, UMR CNRS 6136, Laboratoire des Propriétés Optiques des Matériaux et Applications,
2 Boulevard Lavoisier, 49045 Angers Cedex 01, France*

^aUniversité de Rennes 1, UMR CNRS 6226, Sciences chimiques de Rennes, Campus de Beaulieu, 35042 Rennes Cedex, France

^bAGH University of Science and Technology, WFiIS, al.Mickiewicza 30, 30-059 Krakow, Poland

In this paper we present the first results concerning the Third Harmonic Generation (THG) for thin films of functionalized alkynyl ruthenium based chromophores. This approach allowed us to determine the electronic contribution of the third-order nonlinear optical susceptibility $\chi_{elec}^{<3>}$ of these chromophores and to investigate three theoretical models (Reintjes model, Kubodera and Kobayashi model, and Kajzar and Messier model) as valuable approximations for transcribing the observed results. The highest value of third-order susceptibility found for studied compounds was equal to $\chi_{elec}^{<3>} = 3.0 \times 10^{-20} \text{ m}^2/\text{V}^2$ (at the wavelength $\lambda_0 = 1064 \text{ nm}$, pulse duration 15 ps, average energy 1.6 mJ per pulse, pulse repetition frequency 10 Hz).

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1. Introduction

The nano-world is the further level of miniaturisation, beyond sub-micrometer dimensions of contemporary electronics. This booming area of research and development requires other than already employed materials. Molecular compounds, particularly organic π -conjugated systems as well as transition metal complex compounds are very promising candidates for applications in optoelectronic, quantum electronic and optical communications, and in the field of molecular engineering of functional materials [1-6]. For example, all-optical signal processing needs materials with large third-order nonlinear optical features. Alkynyl-metal complexes represent one of the most widely investigated classes of second and third-order nonlinear optical (NLO) metal complexes [7, 8]. The present paper deals with third-order nonlinear optical properties of functionalized alkynyl ruthenium based chromophores. In these dipolar molecules, metal atoms are directly incorporated in the same plane as the π -conjugated pathway, which meets the requirements for the design of push-pull chromophores with large second-harmonic generation (SHG) efficiencies. Like in the other organic conjugated systems, theoretical and experimental studies of alkynyl metal complexes have shown that large second-order hyperpolarizability characterizing the molecular NLO efficiency depends on the strength of the donor and acceptor groups, on the metal and on the extent of the π -conjugated pathway [9, 10].

In this paper, we describe a novel series of donor-acceptor bis-alkynyl ruthenium film forming chromophores. The results of third harmonic generation (THG) by Maker fringes technique are reported.

We also applied three theoretical models namely Reintjes [11], Kubodera and Kobayashi [12-14], and Kajzar and Messier [15, 16], which were proposed to fit numerically the obtained results. These models were developed to determine the NLO properties of materials and particularly the value of $\chi_{elec}^{<3>}$. Good agreement was found within these three models. Nevertheless, our results show that the model of Kajzar and Messier leads to the most accurate fits.

2. THG - Theoretical background

The THG technique is one of the most informative methods for evaluating the electronic contribution of the real part of the third-order nonlinear optical susceptibilities. An advantage of the THG is the response accounting only for the instantaneous electronic contribution, while the Z-scan and DFWM responses are also sensitive to orientational and vibrational effects. The THG is sensitive to ultrafast electronic mechanisms of nonlinear response within femtosecond relaxation times, and it is almost insensitive to slower effects, such as thermal relaxation. Generally, third-order nonlinear optical processes involve the use of a fundamental coherent laser beam of sufficient power density. In this technique, an

incident laser beam of high intensity at the frequency ω interacts with a nonlinear medium and generates an additional beam at a frequency 3ω . The third harmonic beam corresponds to a pure coherent electronic non-linearity. The generation of third harmonic is an optical interaction of three photons of $h\nu$ energy (in our case, $\lambda_{\omega} = 1064$ nm and $h\nu = 1.17$ eV) which interact to give a photon of $3h\nu$ energy. This nonlinear optical coupling is effective only when the principles of conservation of energy and phase matching conditions are satisfied.

The relationship between the nonlinear optical properties of isolated molecules, as calculated by theoretical chemists and the corresponding macroscopic susceptibilities of condensed phases is of interest for many scientists. From the theoretical point of view, optical wave propagation in isotropic nonlinear media was described in 1962 by Bloembergen and Pershan [17].

A few theoretical models, using various approximations, have been developed in order to determine the value of $\chi_{elec}^{<3>}$ from the shape of the curves of Maker fringes obtained by THG technique.

The model of Reintjes was developed in 1984 [7]. In the frame of this model, wave equation is resolved in a homogenous and non-magnetic nonlinear material, what explains the creation of Maker fringes. The third-order nonlinear optical susceptibility is determined by the Eq. (4).

The model of Kubodera and Kobayashi was proposed in 1990 [12-14]. This model compares directly the maximum of amplitudes of light intensities for third harmonic of non-linear medium with those of a reference material, used for its calibration of the experimental setup. The sample actual value of $\chi_{elec}^{<3>}$ is derived by comparing third harmonic peak intensities of the sample (see Eq. (5) and Eq. (6)) and reference fused silica glass (thickness of 1 mm).

The analysis of THG signals in liquids was developed by Kajzar and Messier in 1985 [15] and applied in 1986 to thin films of organic polymers [16]. This model is based on the formalism of plane waves and propagation of the harmonic optical electric fields generated in a nonlinear medium. In case of thin films, the $\chi_{elec}^{<3>}$ value is calculated by the Eq. (7) and Eq. (8).

2.1. Theoretical model of Reintjes

If one considers an incident monochromatic electric field $\vec{E}(t) = \vec{E}_0 \cos(\omega t)$, the nonlinear polarization which appears and can be written as following [11]:

$$\vec{P}^{<3>}(t) = \chi^{<3>} \vec{E}^3(t) = 1/4 \chi^{<3>} \vec{E}_0^3 \cos(3\omega t) + 3/4 \chi^{<3>} \vec{E}_0 \cos(\omega t) \quad (1)$$

The first term describes a response to frequency 3ω caused by incidental field applied to frequency ω . The second term describes a nonlinear contribution of polarization to frequency ω of incidental field corresponding to dependence with refractive index of medium.

The Maker fringes (see Fig. 1) result from variation of optical way in NLO sample undergoing rotational movement.

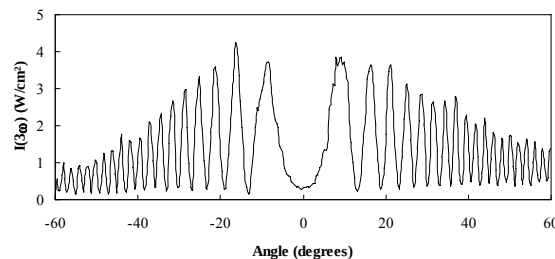


Fig. 1. Typical example of Maker fringes for a sample of silica (reference sample).

Maker fringes become tighter when the angle of incidence $|\theta_i|$ increases because the length of optical way in sample increases non linearly with $|\theta_i|$, whereas intensity of fringes decreases due to increase of reflection coefficient.

The $I_{3\omega}$ intensity is a function of θ_i and the length of optical way (L) in sample, given by:

$$L = d / \cos \theta_i = d / \cos [\arcsin(\sin \theta_i / n_0)] \quad (2)$$

where d stands for the thickness of material and n_0 the refractive index.

The variation of optical way involves dephasing $\Delta\Psi$ between the bound ω wave and the free 3ω wave. The bound ω wave is described by electric field which propagates in nonlinear medium at the same velocity as the fundamental wave. Its velocity is proportional to the refractive index n_ω . The free 3ω wave propagates at a velocity which depends on $n_{3\omega}$.

In absence of absorption and diffusion, the $I_{3\omega}$ intensity depends on dephasing $\Delta\Psi$ between both waves:

$$\Delta\Psi = \Delta k L = (6\pi \Delta n / \lambda_\omega) L = (\pi / L_c) L \quad \text{with} \quad \Delta n = |n_{3\omega} - n_\omega| \quad (3)$$

where λ_ω is the fundamental wavelength and L_c the length of coherence, which corresponds to distance along which bound and free waves gains a phase difference equal to π .

Finally, the TH intensity describes the relation:

$$I_{3\omega} = \frac{576 \pi^6}{n_{3\omega} (n_\omega)^3 (\lambda_\omega)^2 c^2} (\chi_{elec}^{<3>})^2 (I_\omega)^3 L^2 \left(\frac{\sin\left(\frac{\pi L}{2L_c}\right)}{\frac{\pi L}{2L_c}} \right)^2 \quad (4)$$

2.2. Theoretical model of Kubodera and Kobayashi

This model gives the order of magnitude of the third-order nonlinear susceptibility $\chi_{elec}^{<3>}$. The refractive indices and third-order susceptibility are considered real, so the weak absorption of a typical nonlinear sample and the third-order nonlinear susceptibility to the substrate are ignored. The used relation is [12-14]:

$$\chi_{elec}^{<3>} = \chi_S^{<3>} \left(\frac{2}{\pi} \right) \left(\frac{L_{C,S}}{l} \right) \sqrt{\frac{I^{3\omega}}{I_S^{3\omega}}} \quad (5)$$

with $\chi_S^{<3>} = 2.0 \times 10^{-22} \text{ m}^2/\text{V}^2$ [18, 19] (at $\lambda_\omega = 1064 \text{ nm}$) for the thin film or amorphous material whose thickness l is much smaller than the coherence length $L_{C,S}$ of fused silica. This relation adapted for non-zero absorption in the sample becomes:

$$\chi_{elec}^{<3>} = \chi_S^{<3>} \left(\frac{2}{\pi} \right) L_{C,S} \frac{\alpha/2}{1 - e^{-(\alpha l/2)}} \sqrt{\frac{I^{3\omega}}{I_S^{3\omega}}} \quad (6)$$

where $I^{3\omega}$ is the third harmonic peak intensity and α the harmonic absorption loss.

2.3. Theoretical model of Kajzar and Messier

In the case of thin film deposited on a glass substrate and placed in the air (see Fig. 2), one obtains for the resulting electrical field [13, 15, 16]:

$$E_{3\omega}^R = E_S^{3\omega} t_3^{3\omega} + E_F^{3\omega} (t_1^\omega)^3 \quad (7)$$

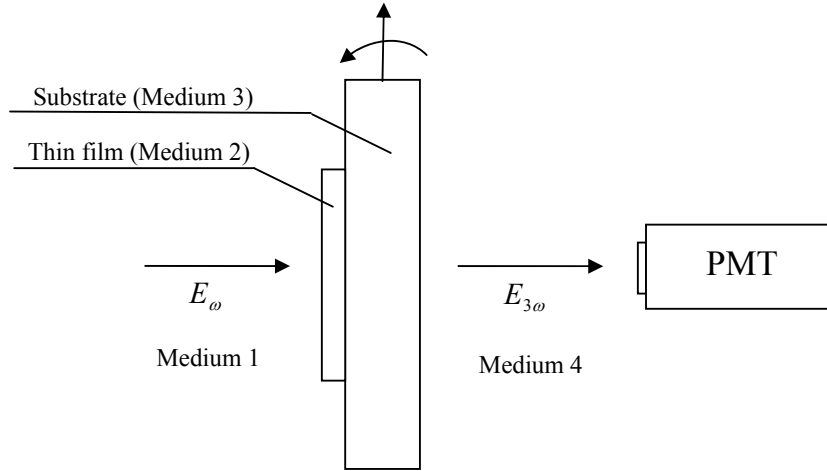


Fig. 2. Disposition of sample including thin film deposited on a glass substrate.

The indices S and F correspond to substrate and thin film, respectively, t_1^ω is the transmission factor of fundamental wave between air and thin film and $t_3^{3\omega}$ is the transmission factor of harmonic wave between substrate and air.

For a transparent thin film, one can obtain for the harmonic intensity:

$$I^{3\omega} = \frac{64\pi^4}{c^2} \left| \frac{\chi^{<3>}}{\Delta\epsilon} \right|_S^2 (I^\omega)^3 \left| e^{i(\psi_S^\omega + \psi_F^\omega)} [T_1(e^{i\Delta\psi_S} - 1) + \rho e^{i\theta} T_2(1 - e^{-i\Delta\psi_F})] + C_{av} \right|^2 \quad (8)$$

with:

$$\rho e^{i\phi} = \left[\frac{\chi_{elec}^{<3>}}{\Delta\epsilon} \right]_F \left/ \left[\frac{\chi^{<3>}}{\Delta\epsilon} \right]_S \right.$$

$$\Delta\epsilon_S = \epsilon_S^\omega - \epsilon_S^{3\omega} = 7.753 \times 10^{-2} \text{ F/m} \quad \text{and} \quad \Delta\epsilon_F = \epsilon_F^\omega - \epsilon_F^{3\omega}.$$

Here $\Delta\epsilon_S$ and $\Delta\epsilon_F$ indicate the dispersion of dielectric constant in substrate and thin film, respectively.

The difference of angles of phase $\Delta\psi_S$ and $\Delta\psi_F$ in substrate and thin film, respectively, can be written in the form:

$$\Delta\psi_S = \psi_S^\omega - \psi_S^{3\omega} = (3\omega l_S / c) (n_S^\omega \cos \theta_S^\omega - n_S^{3\omega} \cos \theta_S^{3\omega}) \quad (9)$$

$$\Delta\psi_F = \psi_F^\omega - \psi_F^{3\omega} = (3\omega l_F / c) (n_F^\omega \cos \theta_F^\omega - n_F^{3\omega} \cos \theta_F^{3\omega}) \quad (10)$$

where l_S and l_F are thickness of substrate and thin film, respectively.

The introduced factors are defined by:

$$T_1 = (t_{12}^\omega t_{23}^\omega)^3 \frac{N_2^{3\omega} + N_2^\omega}{N_2^{3\omega} + N_3^{3\omega}} \quad \text{and} \quad T_2 = (t_{12}^\omega)^3 t_{34}^{3\omega} \frac{N_3^{3\omega} + N_3^\omega}{N_3^{3\omega} + N_4^{3\omega}} \quad (11)$$

with $N_j^{\omega,3\omega} = n_j^{\omega,3\omega} \cos \theta_j^{\omega,3\omega}$ ($j = 1, 2, 3, 4$).

The transmission factors $t_{ij}^{\omega,3\omega}$ for fundamental or harmonic wave (*ss*-polarization) between media i and j are given by the relations:

$$t_{12}^\omega = \frac{2n_1 \cos \theta_1}{n_1 \cos \theta_1 + n_2^\omega \cos \theta_2^\omega} \quad (12)$$

$$t_{23}^\omega = \frac{2n_2^\omega \cos \theta_2^\omega}{n_2^\omega \cos \theta_2^\omega + n_3^\omega \cos \theta_3^\omega} \quad (13)$$

$$t_{23}^{3\omega} = \frac{2n_2^{3\omega} \cos \theta_2^{3\omega}}{n_2^{3\omega} \cos \theta_2^{3\omega} + n_3^{3\omega} \cos \theta_3^{3\omega}} \quad (14)$$

$$t_{34}^\omega = \frac{2n_3^\omega \cos \theta_3^\omega}{n_3^\omega \cos \theta_3^\omega + n_4^\omega \cos \theta_4^\omega} \quad (15)$$

$$t_{34}^{3\omega} = \frac{2n_3^{3\omega} \cos \theta_3^{3\omega}}{n_3^{3\omega} \cos \theta_3^{3\omega} + n_4^{3\omega} \cos \theta_4^{3\omega}} \quad (16)$$

The dispersion of refractive indices Δn_{air} , Δn_S and Δn_F of air, substrate and thin film are defined by:

$$\Delta n_{air} = n_{air}^\omega - n_{air}^{3\omega} = 1.085 \times 10^{-5} \quad (17)$$

$$\Delta n_S = n_S^\omega - n_S^{3\omega} = 2.65 \times 10^{-2} \quad (18)$$

$$\Delta n_F = n_F^\omega - n_F^{3\omega} \quad (19)$$

For fundamental wave at 1064 nm, one knows the values of $\chi_S^{<3>}$ and $\chi_{air}^{<3>}$ [15, 18, 19]:

$$\chi_S^{<3>} = 1.4 \times 10^{-14} \text{ esu} \quad \text{and} \quad \chi_{air}^{<3>} = 7.0 \times 10^{-18} \text{ esu}$$

The factor of air compared to vacuum C_{air} is written in the form:

$$C_{air} = 0.24 C' \left[t_{23}^{3\omega} t_{34}^{3\omega} e^{i(\psi+\alpha)} - (t_{12}^{3\omega} t_{23}^{3\omega} t_{34}^{3\omega})^3 e^{-i(\psi+\beta)} \right] \quad (20)$$

$$\text{with: } C' = \left[\frac{\chi^{<3>}}{\Delta \varepsilon} \right]_{air} / \left[\frac{\chi^{<3>}}{\Delta \varepsilon} \right]_S \quad (21)$$

where ψ corresponds to the phase of air contribution factor, α the difference of phase on the incident side of sample, and $\beta = \alpha + \Delta\psi_S$ the difference of phase on the exit side (between fundamental and harmonic waves for the air propagation).

3. Experimental part

Previously we reported a series of donor- π -acceptor alkynyl ruthenium chromophores built around thiophene based spacers [20,21]. Comparison of the linear and third-order nonlinear optical properties of these donor- π -acceptor chromophores showed that the elongation of the oligothiophene based spacer or further introduction of a double bond leading to a dithienylethylene spacer enhances dramatically the molecular cubic hyperpolarizability. Pursuing this research, a novel series of bis-alkynyl ruthenium chromophores was synthesized and asymmetrically functionalized around the ruthenium centre. Their structure consists of donor group (N,N-dibutylamine), conjugated spacer (azobenzene moiety and ruthenium complex) and acceptor (formyl group). The complex containing ruthenium atom not only gives good

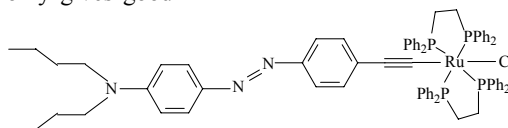
stability, but also participates to electronic transfer along the complete conjugated system. The chemical structures of investigated chromophores are presented in Fig. 3.

Although in terms of transparency azobenzenes are not promising candidates, substituted azobenzene derivatives were chosen because they combine several advantages as: their accessibility and reasonable stability to light and heat and are very interesting for the creation of optical surface gratings [22,23].

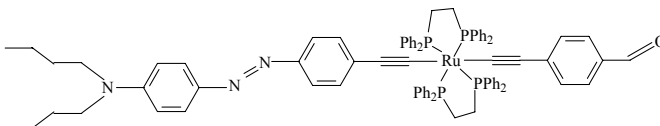
The synthetic methodologies employed for the preparation of the new ruthenium derivatives have been adapted from previously reported procedures [20]. The azo bearing acetylene required for the syntheses of the alkynyl complexes **A-C** was prepared by well-established organic synthetic procedures from its bromo precursor [23]. Complexes **A-C** were isolated as red crystalline powders in approximately 40% yields. All the spectroscopic data of compounds **A-C** are consistent with their proposed structures.

The electrochemical properties of these compounds were measured by means of cyclic voltammetry in dichloromethane solution. Electrochemical data were acquired with a computer-controlled Autolab PG Start 30 potentiostat using the GPES program version 4.7. Electrochemical experiments were performed in a standard three-electrode system (platinum working/auxiliary electrodes and SCE reference electrode) in the presence of internal decamethylferrocene. CH_2Cl_2 solutions containing 10 mg of the studied compound and 0.1M $[\text{n-Bu}_4\text{N}][\text{PF}_6]$ as the supporting electrolyte, 20 °C. Scan rates were typically $200 \text{ mV}\cdot\text{s}^{-1}$. Reversible redox waves of the ruthenium moieties were observed in all the compounds. The half-wave potentials (E_{ox}) of **A**, **B** and **C** were 0.59 V, 0.60 V and 0.60 V, (vs. SCE), respectively. These values are not significantly different from those of the parent compounds as previously described [20].

Complex A
 $\text{C}_{74}\text{H}_{74}\text{ClN}_3\text{P}_4\text{Ru}$



Complex B
 $\text{C}_{83}\text{H}_{79}\text{N}_3\text{OP}_4\text{Ru}$



Complex C
 $\text{C}_{81}\text{H}_{77}\text{N}_3\text{OP}_4\text{RuS}$

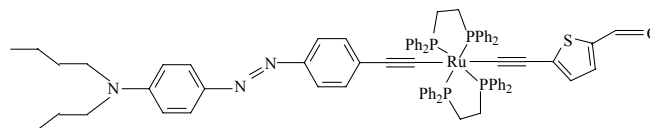


Fig. 3. Chemical structures of studied compounds.

These compounds were deposited on glass substrate of 1 mm thickness by the spin-coating method from

solution in dichloromethane. The thickness of the obtained

thin films was measured with a 6M DEKTAK profilometer and were ranged from 290 nm to 300 nm.

Absorption properties of complexes A-C: The UV-VIS-NIR absorption spectra of the investigated ruthenium complexes are shown in Fig. 4. They were measured both in dichloromethane solution and in thin films using a Lambda 19 PERKIN ELMER spectrophotometer. The physical form had any significant influence on the observed spectrum of a particular chromophore. The values of λ_{max} for thin films of these compounds are given in Table 1. The absorption spectra show broad bands with λ_{max} at 498, 488 and 485 nm for A-C compounds, which were assigned to a superposition of the $\pi-\pi^*$ transition of the azobenzene moieties and of the MLCT (Metal-Ligand-Charge-Transfer) transitions of the alkynyl ruthenium fragments [24, 25].

Table 1. Parameters M , l , λ_{max} and α_{max} present molar masse, thickness of thin film, wavelength of maximum absorption and linear absorption coefficient, respectively.

Compounds	M [g/mol]	l [nm]	λ_{max} [nm]	α_{max} [10^5 cm^{-1}]
A	1265.36	296	498	1.24
B	1359.42	291	488	0.99
C	1365.38	294	485	0.82

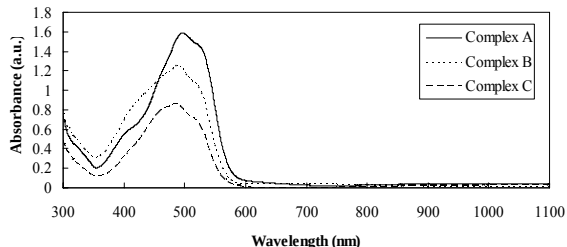


Fig. 4. UV-VIS spectra of the investigated thin films.

The values of linear absorption coefficient α for each investigated compound were evaluated according to Beer-Lambert law (see Table 1).

The voltammetry cyclic technique have been used to determine, in dichloromethane solvent, the HOMO level of the studied compounds from their ionisation potential (I_P). The ionisation potential is calculated using the following relation [26, 27]:

$$I_P = (E_{ox} + 4.4) \text{ eV} \quad (22)$$

The value of ionisation potential is presented, for the studied compounds, in Table 2. In our case, the LUMO level (or electronic affinity) can be deduced only from the difference of both HOMO and optical bandgap (approximately equal to the electrochemical bandgap [27] for our compounds) energies which can be calculated from absorption edges for a thin film as shown in Fig. 5.

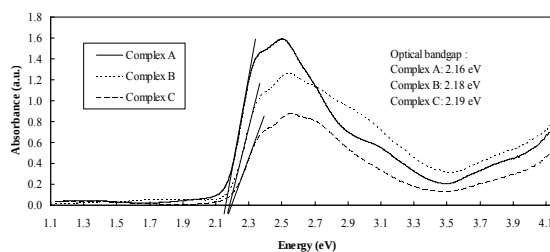


Fig. 5. Values of optical gap for complexes A-C.

Table 2. Electronic structure parameters of studied complexes.

Compounds	HOMO [eV]	Optical bandgap [eV]	LUMO [eV]
A	-4.99	2.16	-2.83
B	-5.00	2.18	-2.82
C	-5.00	2.19	-2.81

The **THG measurements** were carried out for a fundamental wavelength at 1064 nm from a Nd:YAG laser (Model CONTINUUM Leopard D-10) with a pulse duration of 15 ps, and an average energy of 1.6 mJ per pulse at the repetition frequency of 10 Hz. The power of the fundamental beam varied with a half-wave plate which was seated before a Glan-Taylor polarizer (see Fig. 6). The energy of Gaussian fundamental beam was measured with a power-meter (Model OPHIR Nova). The fundamental beam was focused on the sample using a lens which focal distance is equal to about 250 mm. The THG signal was detected by a photomultiplier tube (Model HAMAMATSU R1828-01) and integrated by a box-car, before being processed using LabVIEW program. The sample was rotated by a step motor monitored by a power station of acquisition with an angle resolution up to 0.04° .

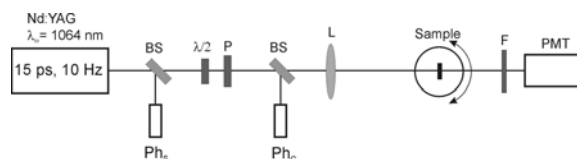


Fig. 6. Experimental setup of THG: BS: beam splitters, $\lambda/2$: half wave plate, P: Glan polarizer, L: convergent lens (250 mm), F: selective spectral filter (355 nm), Phs: synchronization photodiode, Phc: control photodiode, and PMT: photomultiplier tube.

We used a photomultiplier tube with a boarding time of 1.5 ns. The signal of synchronization was given with a photodiode having a boarding time of 20 ns. This photodetector activated the acquisition. An average value on 100 pulses was calculated for each step motor. Each measured point corresponded to the maximum of the amplitude of the I_ω and $I_{3\omega}$ signals (where subscripts ω and 3ω refer to the fundamental and harmonic frequency respectively). One difficulty of this technique is located in the acquisition of THG signal. Indeed, the duration of pulse laser is very short (15 ps) and a power station of

acquisition was made for this study in order to be able to measure this signal. Relaxations of the excitation due to the electron-phonon interactions were neglected.

4. Results and discussion

Thin films, deposited on a thick glass substrate, have been measured and their THG signal was analyzed with fused silica as reference using the Maker fringes technique [28]. Figure 7 shows the Maker fringes patterns of THG observed by rotation of the samples A-C.

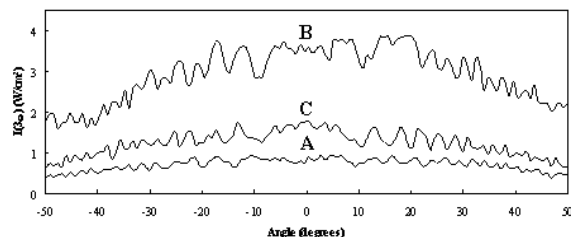


Fig. 7. THG signal dependence as a function of the incident angle of the fundamental beam.

From Fig. 7, one can see non-monotonic angle dependence of the THG signal which reflects a substantial optical non-linearity and this characteristic is typical for all three investigated chromophores.

Experimental values: From these measurements, the power station of acquisition measured and recorded in a file, the values of the incident angle of the fundamental beam, and the output voltage of photodetectors using to detect the light intensities $I_{(\omega,3\omega)}$. For the three theoretical models used in this study, these values allow to extract the NLO coefficients, and particularly the value of $\chi_{elec}^{<3>}$. For each position of the step motor and from the output voltage of photodetectors $V_{S(\omega,3\omega)}$ (in V), we can calculate $I_{(\omega,3\omega)}$ (in W/m²) by the relation:

$$I_{(\omega,3\omega)} = \frac{S_{Ph(\omega,3\omega)} V_{S(\omega,3\omega)}}{\tau (\pi r^2)} \quad (23)$$

where $S_{Ph(\omega,3\omega)}$ is the sensitivity of photodetectors at $\lambda_{(\omega,3\omega)}$ (in J/V), τ the pulse duration ($\tau = 15$ ps), and r the radius of the fundamental beam on the sample ($r = 0.25$ mm).

The investigated alkynyl ruthenium chromophores demonstrate good agreement between the experimental results and the theoretical models. The third-order nonlinear optical susceptibility values for each studied compounds take into account the obtained values of the absorption coefficients. Comparing the measured susceptibilities of the chromophores with the known values for silica (reference material), one can see higher values of the non-linear optical susceptibilities (Table 3).

Among the theoretical models presented, the model of Kajzar and Messier is the most adapted for explaining the experimental values of THG for these organometallic compounds. This model takes into account the majority of parameters which influence the value of $\chi_{elec}^{<3>}$ like the contribution of air and transmission factors on the

interfaces of the nonlinear medium. In our case, the results obtained with two others models give substantially smaller value for $\chi_{elec}^{<3>}$ (see Fig. 8).

Table 3. Results obtained for complexes A-C.

Compounds	$\chi_{elec}^{<3>}$ [10 ⁻²⁰ m ² /V ²]	$\chi_{elec}^{<3>}$ [10 ⁻¹³ esu]	Models
A	0.71	5.09	Reintjes
B	1.45	10.38	
C	1.11	7.95	
A	0.91	6.52	Kubodera and Kobayashi
B	1.92	13.75	
C	1.42	10.17	
A	1.95	13.97	Kajzar and Messier
B	3.01	21.56	
C	2.72	19.19	
Silica (1 mm)	0.02 [18, 19]	0.14	-

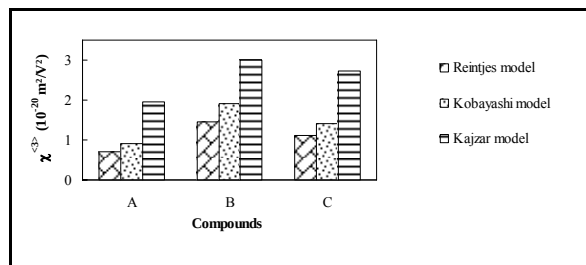


Fig. 8. Comparison of the obtained third-order nonlinear optical susceptibilities using three theoretical models on the studied organometallic compounds.

The compounds **B** and **C** have a larger NLO response than **A** due to the fact that the extent of D-A π -conjugation is clearly much greater in **B** and **C**. Therefore, the third-order nonlinear optical susceptibilities of the largest molecules **B** and **C** are enhanced. The strongest value is observed for the complex **B**: $\chi_{elec}^{<3>} = 3.0 \times 10^{-20}$ m²/V². More crucial is an establishment of a fact that the phenyl-oxygen group gives the maximal effect.

5. Conclusions

In this paper, we evaluated the value of the electronic part of third-order nonlinear optical susceptibility for a new family of functionalized alkynyl ruthenium complexes on thin film. The $\chi_{elec}^{<3>}$ values have been measured using THG method at the fundamental wavelength 1064 nm. We investigated these organometallic complexes in comparing the obtained results with three theoretical models. The results show that these compounds have a $\chi_{elec}^{<3>}$ value approximately larger of two orders of magnitude than the fused silica glass known as reference material. Z-scan measurements will be performed on solutions of these chromophores in order to complete these data.

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*Corresponding author: bouchta.sahraoui@univ-angers.fr