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## *Chapter 6*

# **NONLINEAR OPTICAL PROPERTIES IN IONIC LIQUIDS**

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## **ABSTRACT**

Nowadays it is interesting the huge amount of ionic liquids research that involves their green chemistry and their physical and chemical properties, whilst there has not been a deep research involving their potential applications in optical properties and optoelectronic devices. In this chapter, we show a review of recent research results on this topic, from nonlinear optical properties to potential applications; theoretical and experimental results of common ionic liquids. We also present new experimental results in NLO properties of six ionic liquids. Finally, we summarize some ionic liquids applications in the optical and optoelectronic areas.

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## I. INTRODUCTION

Currently there is a great number of materials which present nonlinear optical properties, some of them are reported in [1-4] but there are few reports on ionic liquids [IL] with nonlinear optical properties. Room Temperature Ionic Liquids (RTILs) are salts composed by bulky organic cations and non-coordinating inorganic anions; they present an ionic-covalent molecular structure and different molecular architectures. They have shown to be excellent solvents for optical investigations of solutes at room temperature with low environmental impact. The IL possesses low melting point temperatures (below 373°K), good electrical conductivity, high ionic mobility, negligible vapor pressure, and excellent chemical and thermal stability. Most of the commonly used ionic liquids are semi-transparent in the UV (>300 nm) and completely transparent in the visible region of light. The most common ionic liquids are based on imidazolium cation, the reason for this is that they are the most studied in many areas. An important feature of IL are their optical properties, these can be linear and nonlinear. For example fluorescence is a linear property and can be applied to sensors design; the fluorescence behavior of some IL depends strongly on the excitation wavelength. However, their nonlinear optical applications are currently unexplored.

The aim of this chapter is to give an overview about nonlinear optical properties of ionic liquids from experimental methods to numerical calculus including molecular and microscopic point of view. Finally, we talk about some potential applications for photonic devices.

At the end of the chapter, (Table 4 and Table 5), we enclose a list of nomenclature and the names of cations and anions of ionic liquids mentioned here.

## II. BRIEF NONLINEAR OPTICAL PROPERTIES THEORY

Light-matter interaction in optics, describes the relation between an electro-magnetic wave and a material, in which the molecular system resides. In the presence of external electric field, all charged particles in the molecule, electrons as well as the atomic nuclei, will experience a force that disrupts their motions. The oscillating charges in the molecule give rise to an induced dipole moment ( $\mu$ ), and the degree to which the external field  $E(t)$  manages to set the charges in motion is expressed as Taylor series

$$\mu(t) = \mu^0 + \alpha E(t) + \frac{1}{2}\beta E^2(t) + \frac{1}{6}\gamma E^3(t) + \dots \quad (1)$$

Where  $\mu^0$  is the permanent electric dipole moment,  $\alpha$  the linear electric polarizability,  $\beta$  the first-order hyperpolarizability,  $\gamma$  the second-order hyperpolarizability, and so forth. In optics, this equation provides the fundamental origin of nonlinearities, and, at the microscopic level, the hyperpolarizabilities govern the nonlinear optics properties performance of the material.

Induced dipolar moment ( $\mu$ ) is a main molecular parameter to analyze due to the fact that it represents all responses, linear and nonlinear, to an external applied electric field ( $E$ , DC or electromagnetic radiation). The linear response of a material is present by changes in linear electric polarizability ( $\alpha$ ) while nonlinear response is present by changes at hyperpolarizability of first ( $\beta$ ) and second ( $\gamma$ ) order.

In macroscopic case, dielectric materials are characterized by their polarization  $P(t)$  of the medium and, if it expands the polarization in orders of the applied external field we have

$$P(t) = P_L + P_{NL} \quad (2)$$

$$P_{NL} = \chi^{(2)}.EE + \chi^{(3)}.EEE + \dots \quad (3)$$

Where  $\chi^{(2)}$  and  $\chi^{(3)}$  are the quadratic and cubic susceptibility parameters respectively that determine the magnitude of the second and third order nonlinear response whose typical phenomena are second -harmonic generation and Kerr (optic and electrooptic) effect respectively [5,6].

In general, third-order optical nonlinear susceptibility  $\chi^{(3)}$  is a complex quantity.

In reference to Kerr optic effect, this is present in a material in which third-order optical nonlinear susceptibility  $\chi^{(3)}$  is non zero, and we can observe their presence in the refraction index changes. These changes can be originated by electronic polarization, molecular orientation, thermal effects, electrostriction, or saturated atomic absorption [7].

Changes in refraction index can be expressed by:

$$n = n_0 + \Delta n \quad (4)$$

And  $\Delta n$  origin, depending on the experimental conditions, can be due to one or multiple mechanisms; one of them is the electronic response of the medium when the rise-up time is shorter than the duration of pulses delivered by the laser source used in the experiments, the other is the thermal effect which is caused by the heating of the medium due to a linear or nonlinear absorption process.

For electronic response (electronic Kerr nonlinearity), the change in the refraction index depends on the optical irradiance,

$$n = n_0 + n_2 I \quad (5)$$

Where  $n_2$  is the nonlinear refraction index, and it is proportional to  $\chi^{(3)}$  and is related by [8]:

$$n_2 = \frac{3\eta_0}{n^2 \epsilon_0} \chi^{(3)} \quad (6)$$

where  $\eta_0 = (\mu_0/\epsilon_0)^{1/2}$ ,  $n$  is the refraction index,  $\epsilon_0$  is the permittivity in free space.

In reference to thermal response of the materials which have low absorption, the change in refractive index is given by:

$$n = n_0 + \frac{dn}{dT} \Delta T \quad (7)$$

Where  $\frac{dn}{dT}$  is the thermo-optic coefficient and  $\Delta T$  is the nonlocal temperature change which depends on the optical fluence [9]

The main difference between this two response is that the electronic response, is local and fast, originated by distortions in electronic cloud due to the electric field which induces changes in optical susceptibility of the medium while the thermal response, is nonlocal, slow and accumulative, originated by heat conduction.

Nonlinear absorption is other interesting property, the absorption depends on the irradiance and nonlinear absorption coefficient ( $\beta$ ) which are related by the equation:

$$\alpha(I) = \alpha + \beta I \quad (8)$$

where  $\alpha$  is the linear absorption coefficient and  $I$  the irradiance of the laser beam.

Nonlinear absorption (NLA) mechanisms are present in one of two forms: Saturable Absorption (SA) or Reverse Saturable Absorption (RSA), RSA that could have been originated by Two-Photon Absorption (TPA), Excited State Absorption (ESA), Free Carrier Absorption (FCA), nonlinear scattering or with the combination of these processes [10-12].

### III. NONLINEAR MEASUREMENT TECHNIQUES

Some common methods to determine nonlinear optical response at microscopic and macroscopic view are respectively, Optically Heterodyned Optical Kerr effect (OHD-OKE), and Z-scan among others.

#### III.1. Optically Heterodyned Optical Kerr Effect (OHD-OKE)

In general, third-order optical nonlinear susceptibility  $\chi^{(3)}$  is a complex quantity. However, for the majority of photonics applications, such as all-optical switching, signal processing, and data storage, the real component of  $\chi^{(3)}$  is more relevant. Unfortunately, in conventional optical Kerr effect (OKE) experiments, the detected signal is proportional to the quadratics of the third-order optical nonlinear susceptibility  $\chi^{(3)}$ . Hence, the real components of  $\chi^{(3)}$  cannot be determined directly from the experiment but, by the introduction of local oscillator field with or without  $90^\circ$  optical phase bias with respect to the optical Kerr signal, a new experimental technique was developed, the optically heterodyned optical Kerr effect (OHD-OKE) [13,14], this new technique allows the determination of the magnitudes and signs of both the real and the imaginary components of  $\chi^{(3)}$  with greatly improved signal-to-noise ratios.

#### III.2. Z-Scan Technique

Z-scan is simple but useful technique that allows to obtain the nonlinear refraction index and nonlinear absorption in only one measurement each.

Bahae developed this technique and their formulism [15], which use a laser beam, a lens aligned with the laser, a sample located in way of the laser after the lens, and a photodetector (example see Figure 1). The mechanism to obtain the information is simple; the sample is displaced along “z axis” across focus of lens while the transmitted light is collected in photodetector. It gives information on transmittance vs displacement “z” and, the curve obtained is characteristic of this technique. Nonlinear absorption characteristic curve using an open aperture and nonlinear refractive characteristic curve using a close aperture in the photodetector can be obtained respectively. Information of NLO properties of the sample can be obtained using different models [15-24] only two are briefly mentioned here:

### III.2.1. Bahae model

The normalized transmittance for close aperture z-scan, is given as:

$$T(z) = 1 + \Delta\Phi_0 \frac{4x}{(1+x^2)(9+x^2)} \quad (9)$$

here  $\Delta\Phi_0 = \frac{2\pi n_2 I_0 L_{eff}}{\lambda}$  is the maximum change phase shift on axis at focus,  $x$  is the dimensionless sample position,  $x = \frac{z}{z_0}$ ,  $z_0 = \frac{\pi\omega_0^2}{\lambda}$  is the Rayleigh parameter of the Gaussian beam with waist  $\omega_0$ ,  $n_2$  is the nonlinear refraction index,  $L_{eff} = (1 - e^{-\alpha L})/\alpha$ , is effective length and  $I_0$  is the irradiance with the sample at the focus ( $z=0$ ).

The normalized transmittance for open aperture z-scan, is given as:

$$T(z) = \frac{\ln[1+q_0(z)]}{q_0(z)} \quad (10)$$

For  $|q_0(z)| < 1$ , where  $q_0(z) = I_0 \beta L_{eff} / (1 + \frac{z^2}{z_0^2})$ .  $\beta$  is the nonlinear absorption coefficient.

### III.2.2. Thermal Lens Model

Aparabolic approximation to the temperature field and an approximation of the optical effects due to temperature, give a behavior to the simple lens [17,18]. The time dependent expression [6] for the far- field on-axis transmittance is:

$$T_N = \frac{I(z,t)}{I(z,0)} = \frac{1}{1 + \left(\frac{\theta}{1+t_c/2t}\right) \left(\frac{zx}{1+x^2}\right) + \left(\frac{\theta}{1+t_c/2t}\right)^2 \left(\frac{1}{1+x^2}\right)} \quad (11)$$

Where  $x = \frac{z}{z_0}$ ,  $z_0 = \frac{\pi\omega^2}{\lambda}$ ,  $t_c = \frac{\omega^2}{4k/C_p} t_c$  is the thermal diffusion time,  $k$  is the thermal conductivity and  $C_p$  is the specific heat per volume at constant pressure. The on-axis phase shift is given by  $= \frac{\alpha PL}{\lambda\kappa} \frac{\partial n}{\partial T}$ , where  $P$  is the power of the Gaussian beam and  $T$  is the temperature. To lower power the nonlinear phase shifts  $\theta \ll 1$ , then the second term of Eq. (5) considering  $t \gg t_c$  is given by

$$T_N = \frac{1}{1 + (\theta) \left(\frac{2x}{1+x^2}\right)} \quad (12)$$

## IV. NONLINEAR OPTICAL PROPERTIES. EXPERIMENTAL DATA

### IV.1 Nonlinear Refraction Index

This section present the experimental data about nonlinear properties of IL as  $n_2$ ,  $\frac{dn}{dT}$ , and  $\chi^{(3)}$ . Studies about nonlinear refraction index of ILs, principally based on imidazolium cation, have been reported. Z-scan technique is the more popular technique to obtain the thermal lens strength ( $\theta$ ), thermo-optical coefficient ( $\frac{dn}{dT}$ ) and nonlinear refraction index  $n_2$ .

Experimental results for ionic liquids where the  $n_2$ , or  $dn/dT$  were determined, have been reported [25-33], a summary of determined values and experimental conditions are show in Table 1.

Souza et al. [25], studied two ionic liquids 1-n-butyl-3-methylimidazolium tetrafluoroborate ([C<sub>4</sub>mim][BF<sub>4</sub>]) and 1-n-butyl-3-methylimidazolium hexafluorophosphate ([C<sub>4</sub>mim][PF<sub>6</sub>]) using two different lasers, they conclude that origin of nonlinearities is thermal and does not present nonlinear absorption. They reported that different ionic liquid structures, determined by the anion, influence the nonlinear refractive index and thermo-optical coefficient dispersion.

Del Sesto et al. [26-28] studied nonlinear optical properties of ionic liquids with tetraalkylphosphonium,  $[\text{PR}_4]^+$  cation, with  $[\text{DTMN}]^{2-}$ ,  $[\text{Co}(\text{NCS})_4]^{2-}$ ,  $[\text{xan}]^-$ ,  $[\text{CoB}]^-$  and  $[\text{DDTC}]^-$  anions, also theoretical calculus of  $\gamma$  anions and cations. They explain that  $[\text{PR}_4]_2[\text{DTMN}]$  has a better nonlinear optical response than  $[\text{PR}_4][\text{DDTC}]$  because it has more sulfur atoms and it is a dianion, as opposed to the DDTC monoanion. The increased response could also be due to having the stronger -CN electron withdrawing group at the opposite end of the anion.

Other researches about NLO in ILs have focused in the analysis of how the cation or anion in ionic liquids develop changes in their linear and nonlinear optical properties that will be discussed in following sections.

### Effects of Anion and Cation in Nonlinear Optical Properties

$(n_2, \frac{dn}{dT})$

As it is well known, increasing the length of N-alkyl substituents at the imidazolium ring of the cation results in an increase in the viscosity of the liquid at any particular temperature, as well as generally increasing the hydrophobic nature of the salt. The introduction of a methyl group at the 2-position on the ring results in a considerable decrease in the polarity of the ionic liquid. Different anions can also give room-temperature ionic liquids of distinctly different characteristics regarding to properties such as viscosity and miscibility with other solvents. Presence of different anion or cation on ionic liquid changes the nonlinear optical properties.

Santos et al. [29,32] studied nonlinear optical properties of ionic liquids with cation using five different derivatives of imidazolium ( $[\text{C}_n\text{mim}]$ ,  $n=4,6,7,10$ ) in two regions: infrared and violet. In infrared region they reported that the ILS with  $[\text{BF}_4]^-$  presented the largest diffusivity while the  $[\text{Tf}_2\text{N}]^-$  gave the smallest result. Similarly, the thermal nonlinear response does not change significantly with cation changes. Nevertheless, the compounds with  $[\text{Tf}_2\text{N}]^-$  have a smaller thermal nonlinear refractive index compared with ILs composed by  $[\text{BF}_4]^-$  and  $[\text{PF}_6]^-$  anions in the near infrared region. The thermo-optical coefficient, and all the measured values, are contained in the range of  $10^{-4} - 10^{-5} \text{ K}^{-1}$ . They reported that  $[\text{C}_4\text{mim}][\text{BF}_4]$  presents the largest value in modulus, while the  $[\text{C}_6\text{mim}]$  and  $[\text{C}_{10}\text{mim}]$  have the smallest results. It was also observed that structures with  $[\text{Tf}_2\text{N}]^-$  as the anion, present lower nonlinear

response in comparison with other ILs with the same cation. Moreover, for a fixed anion  $[\text{Tf}_2\text{N}]^-$  changing the cationic part does not significantly modify the value of the thermal contribution to  $n_2$ . In the purple region they compared the same ILs with the anion  $[\text{Tf}_2\text{N}]^-$  using the chain of imidazolium  $[\text{C}_n\text{mim}]^+$  ( $n=4,6,8,10$ ), they observed that the cationic changes modify the value of the thermal contribution to  $n_2$  from  $-1.8$  to  $-5.1 \times 10^{-8} \text{ cm}^2/\text{W}$  and  $dn/dT$  from  $-2.5$  to  $-12.2 \times 10^{-5} \text{ K}^{-1}$ .

Novoa-Lopez et al.[30] reported their results of ILs (methyl-imidazolium, pyridinium families) analysis about thermal refraction; they mentioned, it is highly sensitive to anionic part of the IL, at reference to thermal conductivity and, confirm that the nature of the cation has only a slight influence on the thermal conductivity of the IL, Furthermore, the anion exerts the strongest influence on physical properties, as it has been observed. In particular  $[\text{BF}_4]^-$  gives rise to higher thermal conductivities(thermo-optic coefficient) than  $[\text{Tf}_2\text{N}]^-$  when combined with the same cation, furthermore, while longer is chain ( $n$ ) in cation  $[\text{C}_n\text{mim}]^+$  with the  $[\text{BF}_4]^-$  anion, the thermo-optic coefficient increases, not as  $[\text{Tf}_2\text{N}]^-$  anion.

Tran et al. [31] studied the thermal lens sensitivity, that is directly related to thermal lens strength ( $\theta$ ) [34] and thermo-optical coefficient ( $\frac{dn}{dT}$ ), to ILs with  $[\text{Tf}_2\text{N}]^-$  anion and different cations as  $[\text{C}_n\text{mim}]^+$  with  $n=2,4,5,6,8$  and different anion as  $[\text{BF}_4]^-$ ,  $[\text{PF}_6]^-$  and  $[\text{Tf}_2\text{N}]^-$ . They found that  $\theta$  is higher in ion  $[\text{PF}_6]^-$  and lower in  $[\text{Tf}_2\text{N}]^-$  using the same  $[\text{C}_4\text{mim}]^+$  cation, respect to the same anion the results shown they found that increasing the chain length of the alkyl group on the imidazolium cation led to an increase in the sensitivity, which means  $\theta$  increase.

In summary, the works that have studied the anion and cation effects over the nonlinear optical properties in ionic liquids, match in that the ionic liquids with cation imidazolium, present a higher nonlinearity when the anion is  $[\text{BF}_4]^-$  than when the anion is  $[\text{Tf}_2\text{N}]^-$ , whilst in some cases the changes in the ( $n$ ) cation chain length with the same anions, increase the nonlinearity.

Valencia et al. [33], used four ionic liquids with same cation methylpyrrolidine and different anion as  $[\text{HNO}_3]$ ,  $[\text{HSO}_4]$ ,  $[\text{HCOO}]$  and  $[\text{CH}_3\text{COO}]$ , they found that  $[\text{CH}_3\text{COO}]$  presents a good nonlinearity compared to other anions. Their values are bigger than others reported to dyes by [35].

Other studies about cation's effect were reported by Xia [36] who reports the effect of symmetry on the low-frequency spectra of imidazolium ionic liquids.

**Table 1. Experimental values of  $n_2$  or  $dn/dT$  to several ionic liquids**

Ionic liquid	$\alpha_o$ ( $\text{cm}^{-1}$ )	Characteristics laser $\lambda$ - $\tau$ - $\nu$	$-dn/dT$ , ( $10^{-5} \text{ } ^\circ\text{K}^{-1}$ )	$-n_2$ ( $10^{-10}$ $\text{cm}^2/\text{W}$ )
[C <sub>2</sub> mim] [BF <sub>4</sub> ] [30]	0.081	810nm-80 fs-80.75 MHZ	1.1	NA
[C <sub>2</sub> mim] [BF <sub>4</sub> ][37]	0.25	514nm-CW-Argon	NA	45.5
[C <sub>2</sub> mim] [Tf <sub>2</sub> N][30]	0.173	810nm-80 fs-80.75 MHZ	0.4	NA
[C <sub>2</sub> mim] [Tf <sub>2</sub> N][37]	0.019	514nm-CW- Argon	NA	25
[C <sub>2</sub> mim] [EtSO <sub>4</sub> ] [30]	0.025	810nm-80 fs-80.75 MHZ	2.8	NA
[C <sub>4</sub> mim] [BF <sub>4</sub> ]	0.015	810nm-80 fs-80.75 MHZ	4.8[30], 75.4[31]	NA
[C <sub>4</sub> mim] [Tf <sub>2</sub> N]	0.049	810nm-80 fs-80.75 MHZ	1.1[30], 40.2[31]	NA
[C <sub>4</sub> mim] [Tf <sub>2</sub> N][37]	0.0194	514nm-CW- Argon	NA	33.9
[C <sub>4</sub> mim] [BF <sub>4</sub> ][ 25]	0.014	810nm-200 fs-76 MHZ	20±6	18±5
[C <sub>4</sub> mim] [BF <sub>4</sub> ][25]	0.29,	514nm-CW- Argon	104	28
[C <sub>4</sub> mim] [PF <sub>6</sub> ][25]	0.032	810nm-200 fs-76 MHZ	8.1±2.4	27±8
[C <sub>4</sub> mim] [PF <sub>6</sub> ][25]	0.054	514nm-CW- Argon	105	97
[C <sub>4</sub> mim][ Tf <sub>2</sub> N] [29]	0.005	820nm-200 fs-76 MHZ	6.0±1.8	4.0±1.2
[C <sub>4</sub> mim][ Tf <sub>2</sub> N] [32]	0.161	410nm-200 fs- (100Hz-1KHz)	9.6±2.9	390±120
[C <sub>6</sub> mim] [Tf <sub>2</sub> N][30]	0.059	810nm-80 fs-80.75 MHZ	0.9	NA
[C <sub>6</sub> mim] [Tf <sub>2</sub> N] [29]	0.012	820nm-200 fs-76 MHZ	3.0±0.9	4.9±1.5
[C <sub>6</sub> mim] [Tf <sub>2</sub> N][32]	0.071	410nm-200 fs- (100Hz-1KHz)	9.3±2.8	190±60
[C <sub>6</sub> mim] [BF <sub>4</sub> ][30]	0.03	810nm-80 fs-80.75 MHZ	25	NA
[C <sub>8</sub> mim] [Tf <sub>2</sub> N][29]	0.007	820nm-200 fs-76 MHZ	7.0±2.1	5.8±1.7
[C <sub>8</sub> mim] [Tf <sub>2</sub> N][32]	0.240	410nm-200 fs- (100Hz-1KHz)	12.2±3.7	510±150
[C <sub>8</sub> mim] [BF <sub>4</sub> ][30]	<0.03	810nm-80 fs-80.75 MHZ	34	NA
[C <sub>10</sub> mim.] [Tf <sub>2</sub> N][29]	0.012	820nm-200 fs-76 MHZ	3.0±0.9	4.7±1.4
[C <sub>10</sub> mim] [Tf <sub>2</sub> N][32]	0.319	410nm-200 fs- (100Hz-1KHz)	2.5±.08	180±50

Ionic liquid	$\alpha_o$ ( $\text{cm}^{-1}$ )	Characteristics laser $\lambda$ - $\tau$ - $\nu$	$-dn/dT$ , ( $10^{-5} \text{ } ^\circ\text{K}^{-1}$ )	$-n_2$ ( $10^{-10}$ $\text{cm}^2/\text{W}$ )
[C <sub>10</sub> mim] [BF <sub>4</sub> ][30]	0.03	810nm-80 fs-80.75 MHZ	45	NA
[C <sub>12</sub> mim] [Tf <sub>2</sub> N][29]	0.013	820nm-200 fs-76 MHZ	NA	5.0±1.5
[C <sub>4</sub> mim] [MetFSO <sub>4</sub> ] [30]	0.043	810nm-80 fs-80.75 MHZ	1.9	NA
[C <sub>4</sub> C <sub>1</sub> Pyrr] [Tf <sub>2</sub> N][30]	0.039	810nm-80 fs-80.75 MHZ	1.3	NA
[C <sub>6</sub> C <sub>6</sub> C <sub>6</sub> C <sub>14</sub> P] [Tf <sub>2</sub> N][30]	0.074	810nm-80 fs-80.75 MHZ	1.5	NA
[C <sub>2</sub> mim] [CF <sub>3</sub> COO][37]	0.08	514nm-CW- Argon	NA	31.3
[C <sub>4</sub> mim] [CF <sub>3</sub> COO][37]	0.08	514nm-CW- Argon	NA	18
[C <sub>1</sub> C <sub>1</sub> Pyrr] [NO <sub>3</sub> ] [33]	0.95	514nm-CW- Argon	NA	1469
[C <sub>1</sub> C <sub>1</sub> Pyrr] [HSO <sub>4</sub> ] [33]	0.20	514nm-CW- Argon	NA	1636
[C <sub>1</sub> C <sub>1</sub> Pyrr] [HCOO] [33]	<0.02	514nm-CW- Argon	NA	677
[C <sub>1</sub> C <sub>1</sub> Pyrr] [CH <sub>3</sub> COO] [33]	2.4	514nm-CW- Argon	NA	26362
[PR <sub>4</sub> ] [xan][28]	NA	910 nm-3ps-76MHz	NA	0.09
[PR <sub>4</sub> ] [CoCB][28]	NA	910 nm-3ps-76MHz	NA	0.22
[PR <sub>4</sub> ] [DDTC][ 26,28]	NA	910 nm-3ps-76MHz	NA	0.45
[PR <sub>4</sub> ] <sub>2</sub> [Co(NCS) <sub>4</sub> ][28]	NA	910 nm-3ps-76MHz	NA	1.9
[PR <sub>4</sub> ] <sub>2</sub> [DTMN][ 26,27,28]	NA	910 nm-3ps-76MHz	NA	6.1

## IV.2 Nonlinear Absorption

To study nonlinear absorption behavior of ionic liquids, we applied the Z-scan technique; we used an argon laser (514 nm) of variable power, which was focused by an 80 mm focal length lens. The experimental set up scheme used, is shown in Figure 1. The laser beam waist  $\omega_0$  at the focus was measured to be 35  $\mu\text{m}$ , a 20  $\mu\text{m}$  and we used an optical path length cell containing the ionic liquid which was translated across the focal region along the axial direction that is the direction of the propagation laser beam. The transmission of the beam was measured through an aperture placed in the far field using a photodetector fed to the digital power meter.

The nonlinear absorption value of some ionic liquids was determined using [38]:

$$T(z) = 1 - \frac{q_0}{2\sqrt{2}} \frac{1}{[1 + \frac{z^2}{z_0^2}]} \quad (13)$$

Where  $q_0 = \beta I_0 L_{eff}$  with  $|q_0| \ll 1$ .

The ionic liquids  $[C_4mim][TF_2N]$ ,  $[C_2mim][TF_2N]$ ,  $[C_2mim][BF_4]$ ,  $[C_4mim][BF_4]$ ,  $[C_2mim][CF_3COO]$ , and  $[C_4mim][CF_3COO]$  were prepared following literature procedures [39], and synthesized in DCN-UGTO Polymers Laboratory, the absorption spectra of the IL are shown at Figure 2, as it is known, they are transparent at visible.

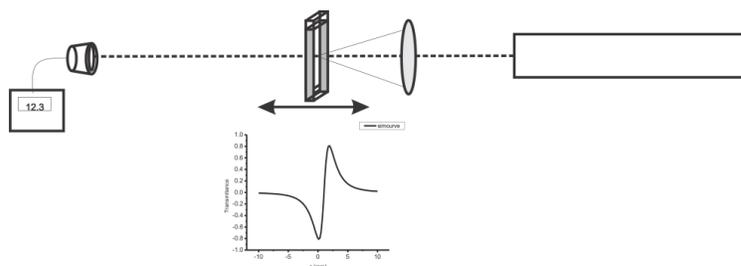


Figure 1. Experimental setup to obtain z-scan curves with open aperture.

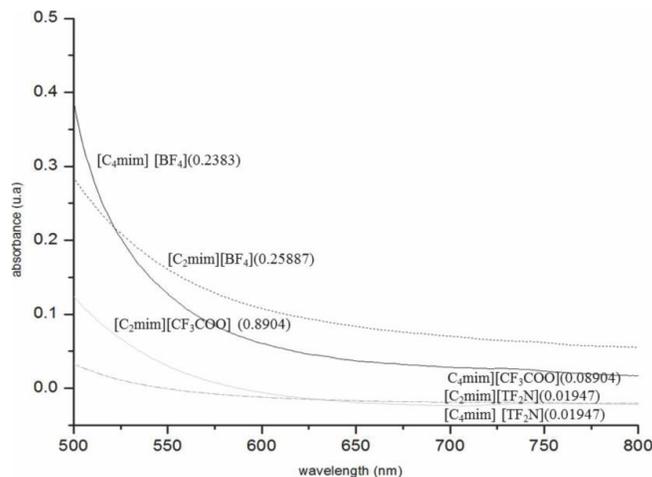


Figure 2. UV-Vis spectra to Ionic liquids.

The refraction curves obtained of ionic liquids, and absorption represented by beta, are shown in Figure 3-5. Figure 3 shows a nonlinear absorption experimental data for  $[C_2mim][BF_4]$  and  $[C_4mim][BF_4]$  ionic liquids note the transmittance was decreasing while the IL was approximated to focus where the input intensity was increased, it is the characteristic behavior of Reverse

Saturable Absorption (RSA) or positive nonlinear absorption.  $[\text{BF}_4]$  anion with different cation present the same nonlinear absorption it practically means that the chain length in cation does not influence this property. We measured using a laser at 632.8 nm at 15 mW of power to  $[\text{C}_4\text{mim}][\text{BF}_4]$  and also presented a RSA behavior. The following ionic liquids  $[\text{C}_2\text{mim}][\text{CF}_3\text{COO}]$  and  $[\text{C}_4\text{mim}][\text{CF}_3\text{COO}]$  (Figure 4) show a remarkable difference because whilst the first presented a minimum at focus like RSA behavior the second presented a maximum at focus, and this corresponds to RSA-SA switch behavior in the same experimental conditions, which means that the cation has a big influence at nonlinear absorption property.  $[\text{C}_2\text{mim}][\text{TF}_2\text{N}]$  and  $[\text{C}_4\text{mim}][\text{TF}_2\text{N}]$  z-scan curves with open aperture are show in Figure 5, they presented an increase at transmittance when ILs are approximate to focus, this means the presence of Saturable Absorption (SA), but note that  $[\text{C}_4\text{mim}][\text{TF}_2\text{N}]$  will be changed to RSA at higher power than 8 mW.

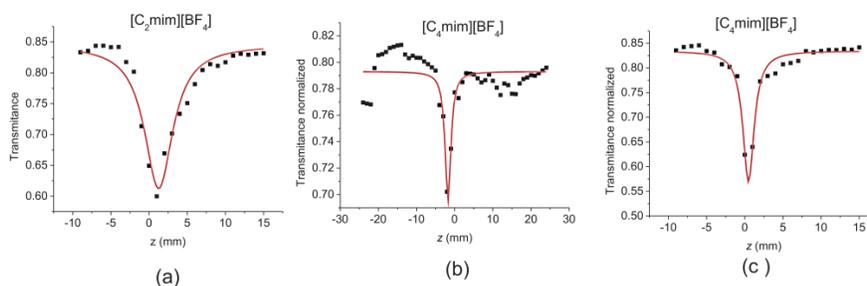


Figure 3. Z-scan curves to ionic liquids with  $[\text{BF}_4]^-$  anion. (a)  $\beta=(62.644\pm 4.1200)\times 10^{-4}$  cm/W (514 nm-100mW), (b)  $\beta=(72.122\pm 6.16927)\times 10^{-4}$  cm/W (514 nm-100mW), (c)  $\beta=(3.54901\pm 0.5723)\times 10^{-4}$  cm/W (632.8 nm-15mW).

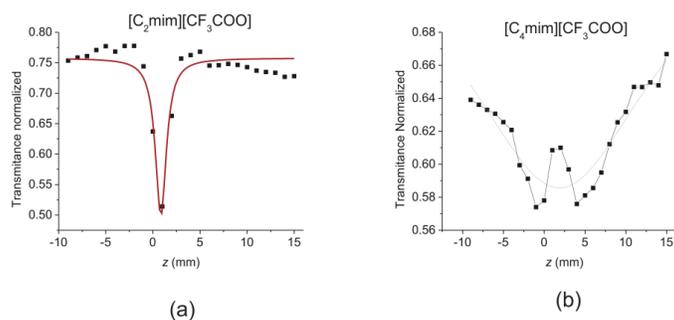


Figure 4. Z-scan curves to ionic liquids with  $[\text{CF}_3\text{COO}]^-$  anion at 514 nm-100mW, (a)  $\beta=(70.6339\pm 8.2297)\times 10^{-4}$  cm/W, (b)  $\beta= \text{NA}$  cm/W.

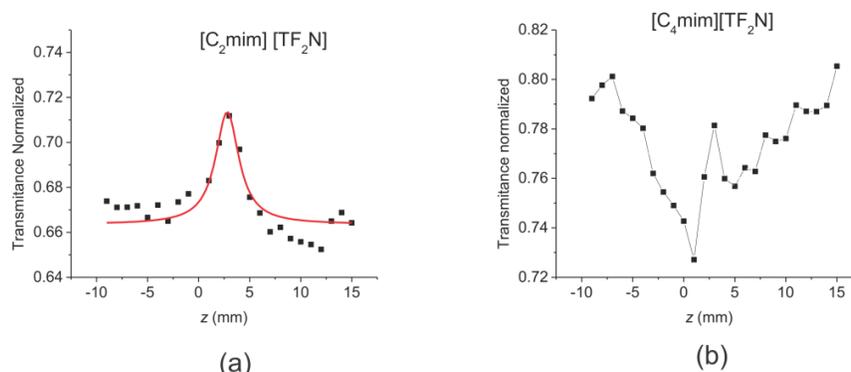


Figure 5. Z-scan curves to ionic liquids with [TF<sub>2</sub>N]<sup>-</sup> anion at 514 nm-100mW  
 (a)  $\beta = (-13.597 \pm 1.79465) \times 10^{-4}$  cm/W, (b)  $\beta = \text{NA}$  cm/W.

The nonlinear optical parameters of presented IL samples, are higher than the reported results under cw regime to dye [35].

## V. NONLINEAR OPTICAL PROPERTIES. THEORETICAL CALCULUS

### V.1 Dielectric Constants

The dielectric constant ( $\epsilon$ ) is extracted from the complex permittivity,  $\epsilon^*(\nu)$ , measurement of a material as a function of the frequency of the applied electric field. The dielectric constant is defined as the zero-frequency of  $\epsilon^*(\nu)$  in the absence of ionic conductivity and thus reflects the contributions from: a) the ionic, distortion and electric polarization caused by the molecular polarizability ( $\alpha$ ) and b) the orientation polarization caused by the permanent dipole moment ( $\mu$ ).

Ionic polarization is known to be of importance in crystalline salts below the IR region. Such ion displacements simply lead to conductive motions in molten salts where the ions are small and mobile. In the case of ionic liquids, small relative displacements of the ions, or parts of the ions may be possible but longer-range motions required for conduction hindered. Hence “ionic polarization” may contribute to the overall polarization in this case. Ionic liquids might also display in some cases an additional component of ionic polarization that originates from distortion of the electron density on the ion

induced by the presence of surrounding ions and results in a slight displacement of charge. This charge displacement can enhance the overall dipole moment of the ion, resulting in a further contribution to the dielectric constant. Thus one may expect that ionic polarization may be a contributor to the polarizability of ionic liquids, at some frequency above the region where ion conduction dominates.

The electronic polarizability is only an amount that easily be calculated by using electronic polarizabilities obtained from *ab initio* theory. Table 2 show some of the theoretical dipole moment calculated ( $\mu/D$ ) [40].

Theoretical studies have been used to determine the second hyperpolarizability ( $\gamma$ ) of some anions or cations. These were based on computational methods and the calculations was done in the gas phase in absence of any counterions or other lattice//structural interactions present. In general, many studies show that organic and molecular inorganic materials need to have an extensive degree of electronic conjugation, leading to highly polarizable electrons, in order to have a large ( $\gamma$ ).

**Table 2. Dipole moment calculated to some ions using *ab initio***

Ion	$\mu/D$
[BF <sub>4</sub> ] <sup>-</sup>	0.000
[PF <sub>6</sub> ] <sup>-</sup>	0.000
[Tf <sub>2</sub> N] <sup>-</sup> ( <i>cis</i> )	3.6902
[Tf <sub>2</sub> N] <sup>-</sup> ( <i>trans</i> )	0.299
[EtSO <sub>4</sub> ] <sup>-</sup>	5.791
[Cl] <sup>-</sup>	0.000
[N(CN) <sub>2</sub> ] <sup>-</sup>	0.000
[CF <sub>3</sub> COO] <sup>-</sup>	6.679
[NO <sub>3</sub> ] <sup>-</sup>	0.000
[C <sub>2</sub> mim] <sup>+</sup>	1.622

Yeates et al. [41] studied the second hyperpolarizability ( $\gamma$ ) using *ab initio* Hartree-Fock protocols of some anions as: Trithiocarbonate, xanthate, Acinitro-dithioacetate (K-salt), aci-nitrodiselenoacetate and melonitrile, and some ionic liquids formed by k-salt anion and cations as: Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> and MEI<sup>+</sup>. They optimized the geometry of anions using the Restricted Hartree-Fock (RHF) level of theory with Dunning-Hay basis set enhanced with polarization and diffuse *sp* functions. The second hyperpolarizabilities of the anions were computed with finite-field method using the same basis except the diffuse *sp*

functions were replaced with the set of diffuse p and d functions designed for NLO computations. They computationally show how there is an enhanced hyperpolarizability from increasing the electron density in the “diffuse” region. And they mention that anions containing higher row elements demonstrate to be a promising expression on this new structure-property relationship. Del Sesto et al. [27] in their chapter calculate the second hyperpolarizability ( $\gamma$ ) to some anions using the Restricted Hartree-Fock (RHF) and MP2 protocols (see Table 3). They report the effects of higher row elements which increase the negative charges on  $\gamma$  values of anions and mentioned that the presence of cation due their high charge density can decrease the polarizability of the diffused anions. According to Table 3, monoanions with third row elements (e.g.,  $[\text{HOCS}_2]^-$ ) have higher gammas than monoanions with second row elements (e.g.,  $[\text{HCO}_2]^-$ ) and dianions containing sulfur ( $[\text{O}_2\text{NCHCS}_2]^{2-}$ ) have highest gamma values. They mentioned that the presence of cation due their high charge density can decrease the polarizability of the diffuse anions.

**Table 3. Theoretical values to some anions using Restricted Hartree-Fock (RHF) and MP2 protocols**

Anion	$\gamma \times 10^{-3}$ a.u (RHF)
$[\text{CS}_3]^{2-}$	299[40]
$[\text{OS}_3]^{2-}$	50[40]
$[\text{HCS}_3]^-$	76[40]
$[\text{HCO}_3]^-$	8[40]
$[\text{H}_2\text{CS}_3]$	20[40]
$[\text{O}_2\text{NCHCSe}_2]^{2-}$	408[40]
$[\text{NO}_2]^-$	9[27]
$[\text{HCO}_2]^-$	12[27]
$[\text{HOCS}_2]^-$	66[40,27]
$[\text{H}_2\text{NCS}_2]^-$	84[27]
$[\text{O}_2\text{NCHCS}_2]^{2-}$	268[40,27]
$[(\text{NCCS})_2]^{2-}$	435[40,27]
Ionic liquid	
$[\text{Li}]_2[\text{O}_2\text{NCHCS}_2]$	42[40]
$[\text{Na}]_2[\text{O}_2\text{NCHCS}_2]$	71[40]
$[\text{K}]_2[\text{O}_2\text{NCHCS}_2]$	119[40]
$[\text{MEI}][\text{O}_2\text{NCHCS}_2]$	66[40]

**Table 4. List of names of anions of ILs**

Short name anion	Long name anion
$[\text{BF}_4]^-$	Tetrafluoroborate
$[\text{PF}_6]^-$	Hexafluorophosphate
$[\text{Tf}_2\text{N}]^-$	Bis(trifluoromethylsulfonyl) imide
$[\text{EtSO}_4]^-$	Ethyl Sulfate
$[\text{SbF}_6]^-$	Hexafluoroantimonate
$[\text{MetSO}_4]^-$	Methylsulfate
$[\text{MetFSO}_4]^-$	Triflate
$[\text{Cl}]^-$	Chloride
$[\text{N}(\text{CN})_2]^-$	Dicyanamide
$[\text{Br}]^-$	Bromide
$[\text{CF}_3\text{COO}]^-$	Trifluoroacetate
$[\text{NO}_3]^-$	Nitrate
$[\text{HSO}_4]^-$	Hydrogen sulfate
$[\text{HCOO}]^-$	Formate
$[\text{CH}_3\text{COO}]^-$	Acetate
$[\text{DTMN}]^-$	Methyl xanthate
$[\text{DDTC}]^-$	Dietyldithiocarbamate
$[\text{CoCB}]^-$	Bis(dicarbollyl)cobalt(III)
$[\text{Co}(\text{NCS})_4]^-$	Tetrathiocyanocobaltate(II)
$[\text{HOCS}_2]^-$	Xanthate
$[\text{CS}_3]^{2-}$	Trithiocarbonate
$[\text{OS}_3]^{2-}$	Yeates
$[\text{HCS}_3]^-$	Hydrogen Trithiocarbonate
$[\text{HCO}_3]^-$	Hydrogen carbonate
$[\text{H}_2\text{CS}_3]^-$	Acid Trithiocarbonic
$[\text{O}_2\text{NCHCSe}_2]^{2-}$	Acid nitrodiselenoacetate
$[\text{NO}_2]^-$	Nitrium
$[\text{HCO}_2]^-$	Hydrogen carbonaceous
$[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$	N-bis(trifluoromethanesulfonyl)
$[\text{H}_2\text{NCS}_2]^-$	yeates
$[\text{O}_2\text{NCHCS}_2]^{2-}$	Aci-nitro-dithioacetate (K-salt)
$[(\text{NCCS})_2]^{2-}$	melonitrile

## V.2 Ionic Liquid Crystalline Polymer

Some ionic liquid crystalline polymers, as azobenzene ionic liquid crystalline polymer, have been studied. This compound presents nonlinear optical properties and has been studied in solution or thin film, using different techniques as z-scan [42], and OKE and pump-probe techniques [43], nonlinear refraction index value for polymer thin film is  $n_2 = -1.07 \times 10^{-9} \text{ cm}^2/\text{W}$  and nonlinear absorption index is  $\beta = -0.72 \times 10^4 \text{ cm/GW}$ , were determined using a picosecond laser at 532 nm and z-scan technique also the third order nonlinear susceptibility  $\gamma = 8.26 \times 10^{-10} \text{ esu}$  was determined using OKE and pump-probe techniques, using femtosecond laser pulse generated from a mode-locked Ti:Sapphire oscillator generating 100 fs at 800 nm, with time response as 300 fs; in solution the third order nonlinear susceptibility  $\gamma = 2.1 \times 10^{-14} \text{ esu}$  that corresponds to a second hyperpolarizability  $\chi^{(3)} = 2.3 \times 10^{-32} \text{ esu}$  at concentration of  $2 \times 10^{-3} \text{ M}$  was determined.

## VI. APPLICATIONS

Modern optical technologies demands improving the ability to control the light, as phase, or intensity to fit, to control, and modify certain new devices. The knowledge of optical properties, such as chromatic dispersion, thermal refraction, linear and nonlinear absorption, and reflectivity, among others, is crucial to design, to manufacture and for the correct operation of a photonic an optoelectronic components. Ionic liquids have a great chance to be used to develop new devices for mainly two reasons: they are considered part of green chemistry which is necessary to contribute to avoid the electronic contamination and because they possess good nonlinear optical properties.

Some Ionics liquids have potential applications as optical limiters, because they exhibit a linear transmission below a threshold and clamps the output to a constant above it. This phenomenon can be achieved by one or more of the nonlinear optical mechanisms such as excited state absorption (ESA), free-carrier absorption (FCA), two photon absorption (TPA), thermal defocusing/scattering, photorefraction, nonlinear refraction, and induced scattering [44].

Ionic liquids are used as plasticizers to develop ion optodes [45], the possibility then exists for using the nonlinear optical properties of ionic liquids to improve optodes or sensors. On the other hand, ionic liquids can be used as

solvents to measure thermal nonlinearity of analytes, it has been observed that ILs enhance the sensitivity of measure the thermal nonlinearity and this is due to their relatively better thermo-optical properties [46].

**Table 5. List of names of cations of ILs**

Short name cation	Long name cation
[C <sub>n</sub> mim] with n=2,4,5,6,8,10	1-C <sub>n</sub> -3-methylimidazolium
[C <sub>4</sub> C <sub>1</sub> Pip]	1-Butyl-1-methylpiperidinium
[C <sub>4</sub> Py]	1-Butylpyridinium
[C <sub>1</sub> C <sub>1</sub> Pyrr]	1-Methyl-1-methylpyrrolidinium
[C <sub>4</sub> C <sub>1</sub> Pyrr]	1-Butyl-1-methylpyrrolidinium
[C <sub>6</sub> C <sub>6</sub> C <sub>6</sub> C <sub>14</sub> P]	Trihexyl(tetradecyl)phosphonium
[C <sub>2</sub> C <sub>2</sub> C <sub>2</sub> S]	Triethylsulphonium
[PR <sub>4</sub> ] or [PC <sub>6</sub> C <sub>6</sub> C <sub>6</sub> C <sub>14</sub> ]	Trihexyltetradecylphosphonium
[MEI]	1—methyl-3-ethylimidazolium

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