

# Picosecond measurement of the nonlinear refractive index of new salts of carboxylate anions with chiral ammonium cations

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## Abstract

The third order nonlinear optical properties of novel carboxylate anions with chiral amines and ammonium cations have been studied by a new alternative of the classical *z*-scan technique with picosecond laser pulses (pulse duration of 30 ps at 1064 nm wavelength). The materials do not present linear and nonlinear (two-photon) absorptions at the wavelength and the intensities used for the experiments. The non-resonant molecular second order hyperpolarizability  $\gamma$  obtained can reach  $4.4 \times 10^{-48}$  SI. These values are two and three orders of magnitude larger than those CS<sub>2</sub> and of C<sub>6</sub>H<sub>6</sub> respectively.

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## 1. Introduction

Materials possessing large and fast nonlinear responses combined with good optical quality have attracted a great deal of interest because of their potential applications in optical communications, optical interconnections and integrated optics [1,2].

In particular, the interest in organic materials [3–5] lies not only on their enhanced nonlinear responses over a wide frequency range together with ultrafast response

times and high damage thresholds, but also on the inherent adaptability of their molecular structures and the possibility of film forming and processing. Moreover it is expected that the compounds used to form materials will depend on the particular application and therefore it is likely that there will be a continuous need for designing new molecules for optoelectronics.

In organic materials, there is a strong correlation between structure and nonlinear properties. Thus, in the case of second order nonlinear effects, it has been established that the macroscopic susceptibility of the materials  $\chi^{(2)}$ , is related to both the magnitude of the molecular nonlinearities, i.e. the first hyperpolarizability  $\beta$ , and the relative orientation of the molecules in the medium. Therefore, a fundamental limitation for second-order effects to be observed is the non-centrosymmetry requirement, both at the microscopic molecular level and at

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the macroscopic bulk level. On the other hand, the third order effects described by  $\chi^{(3)}$  can be present in any medium. The  $\chi^{(3)}$  coefficients are thus essential in centrosymmetric compounds where the second order coefficients equal zero. They are also important in the non-centrosymmetric molecules. Moreover, these  $\chi^{(3)}$  coefficients play a part in some experimental determination of  $\chi^{(2)}$  coefficients. It is for example the case in electric field induced second harmonic generation [6–10] (EFISHG) experiment or in hyper-Rayleigh technique [11–16] where the two-photon absorption (TPA), which is third order effect, can induce fluorescence thus making imprecise the determination of the  $\beta$  coefficient.

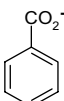
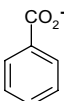
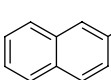
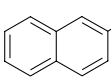
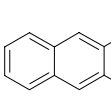
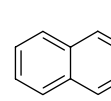
The basis of the choice of the compounds studied in the present work, is the expectation of enhanced (hyper) polarizability of anions relatively to neutral molecules of comparable structures [15]. Thus, these compounds should lead to high second and third order nonlinear optical coefficients.

In a previous work [15], we have studied the second order NLO properties of aromatic thiolates. These stud-

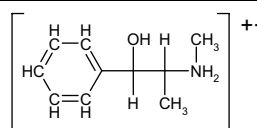
ies showed theoretically and experimentally that this class of material could have great second order nonlinear coefficients (for frequency doubling). But the experiment showed that they were not very stable in time. Now, we are interested to salts **4–6** (see Table 1) of aromatic carboxylate anions which are expected to possess greater chemical stability than the thiolates salts, and also to salt **10** containing the very large and polarizable monoatomic iodide anion. These anions were associated in the case of compound **6** to non-centrosymmetric chiral ephedrinium cations in order to be suitable both for the present third order ( $\chi^{(3)}$ ) nonlinear optical properties study and for second order ( $\chi^{(2)}$ ) measurements which will be presented later.

The paper is organized as follows: in the Section 2, we summarize the materials synthesis technique and in the Section 3, we present the principle of the measurement technique used to determine the third order nonlinear optical coefficients of the materials studied. This technique is based on a newly developed alternative to the classical  $z$ -scan technique. It is better adapted than the

Table 1  
Concentration,  $n_2^{\text{test}}/n_2^{\text{C}_6\text{H}_6}$  and  $\gamma_{\text{molecular}}$  values of the materials studied

Code	Materials	C (g/l)	$\frac{n_2^{\text{sample}}}{n_2^{\text{C}_6\text{H}_6}}$	$\gamma_{\text{mol}} (\times 10^{48}) (\text{m}^5/\text{V}^2)$
1	C <sub>6</sub> H <sub>6</sub> (reference material)		1	$2.60 \times 10^{-2}$
2	CHCl <sub>3</sub>		0.360	$9.30 \times 10^{-3}$
3	CS <sub>2</sub>		3.005	$5.00 \times 10^{-2}$
4	 , N(CH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>	50	0.080	$1.20 \times 10^{-1}$
5	 , Ephedrinium	30	0.177	$6.4 \times 10^{-1}$
6	 , N(CH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>	5.0	0.232	4.4
7	 , Ephedrinium	50	0.129	3.3
8	 , 2N(CH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>	20	0.196	1.4
9	 , 2 Ephedrinium <sup>+</sup>	5.0	0.084	3.21
10	I <sup>-</sup> , Ephedrinium	20	0.129	$7.00 \times 10^{-1}$

Ephedrinium:



classical  $z$ -scan to materials even if they have weak nonlinearities and poor optical quality. These two points will be depicted in Section 3.

In Section 4, we report measurements of the third order nonlinear refractive index in solutions of the synthesized materials and determine the second order hyperpolarizability  $\gamma_s$  of the different molecules studied. The obtained results are analyzed and discussed. Finally, we study the dependence of the nonlinear refractive index on the concentration of the solution.

## 2. Sample preparation

The ephedrinium salts **4** and **5** were obtained through neutralization of the corresponding acids by ephedrin: 10ml of the acid and the stoichiometric amount of the ephedrin (i.e. 10ml in the case of the preparation of **4**, 20ml in the case of **5**) were codissolved in methanol. Afterwards, evaporation of methanol afforded in most cases an oily solid which was crystallized by washing diethyl ether and then vacuum dried.

The tetramethylammonium salt **6** was obtained in same way except that the ephedrin was replaced by a commercial methanolic solution of tetramethylammonium hydroxide whose exact concentration (2.44 mol/l) had been previously determined through acidimetric titration.

The iodide salt **10** was obtained through nucleophilic substitution of iodomethane by *N*-methylephedrine: both reactants were dissolved in diethyl ether. The salt **7** slowly precipitated from this solution and was collected by filtration after 7 days.

These compounds were characterized by resonance magnetic nuclear of protons and absorption spectra. They were shown to be completely transparent to the absorption in the UV–visible near-infrared region of

the spectrum: spectra of solutions in methanol, recorded on an ATI-UNICAM spectrometer in range 250–1100nm show no absorption above 350–400nm. A characteristic absorption spectra is shown in Fig. 1. The structures of the studied compounds and their designation are summarized in Table 1.

## 3. Experimental

Several experimental methods are known for the measurement of the third order nonlinear refractive index ( $n_2$ ) in optical materials [16–27]. Among them, the  $z$ -scan technique introduced by Sheik-Bahae et al. [24,25], has become a standard tool for the determination of sign and magnitude of  $n_2$  because of its experimental simplicity and accuracy. In this technique, a sample is scanned along the optical axis ( $z$ -direction) of a focused Gaussian laser beam. The phase distortion that undergoes the light beam in the nonlinear material is converted to transmission variations through a small aperture located in the far field and centered at the spot. The variation of the transmission with the sample position gives the typical valley-peak (or peak-valley depending on the sign of  $n_2$ ) curve, which leads to the direct determination of the induced nonlinear phase shift and thus to the magnitude and sign of the nonlinear refractive index.

A number of extensions and alternatives of standard  $z$ -scan technique have been then proposed for third order susceptibility  $\chi^{(3)}$  measurements with higher sensitivity [20,21], experimental simplicity [23] and applicability to a wider range of materials [24,26].

In order to measure the third order nonlinear refractive index of the samples described in Section 2, we used a simple alternative to the classical  $z$ -scan technique. Using the typical  $z$ -scan configuration, we fixed the position of the sample and take intensity dependent transmission measurements of solutions of the molecules in the near and far field.

Similarly to  $z$ -scan, the close aperture transmission leads to the sign and magnitude of the  $n_2$  and the open aperture transmittance to the nonlinear absorption.

The principal advantage of this method is that it does not require any mechanical movement during measurement. Consequently, it is particularly suitable to rather quickly test newly synthesized materials.

Now, let us consider a material whose the thickness  $L$  is lower than the Rayleigh length  $z_0$  of the beam [25,28] and suppose that the third order nonlinear susceptibility of this material is a complex quantity

$$\chi^{(3)} = \chi_R^{(3)} + i\chi_I^{(3)} \quad (1)$$

where real part is related to nonlinear refractive index coefficient  $n_2$  and the imaginary part is related to the two-photon absorption  $\beta$ . The physical parameters  $n_2$

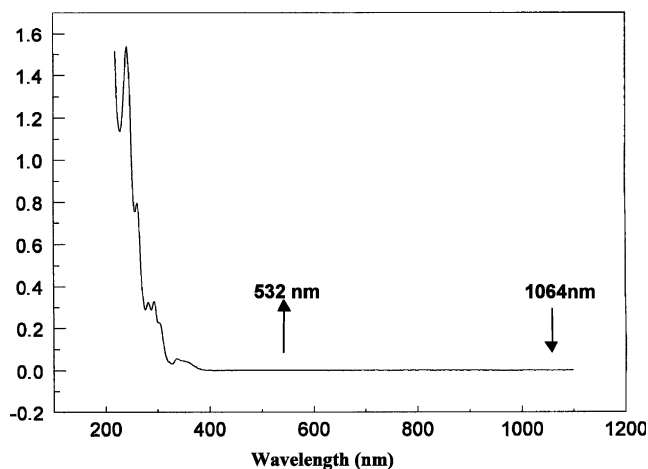


Fig. 1. Absorption spectrum characteristic of the new studied materials with methanol as solvent.

and  $\beta$  are obtained through the close and open normalized transmittances which are noted here  $\Delta T_R$  and  $\Delta T_I$  respectively and are given by the following relations:

$$\Delta T_R = T_R - 1 = -\frac{4kn_2 I_0 L_{\text{eff}} x}{(1+x^2)(9+x^2)} \quad (2)$$

$$\Delta T_I = T_I - 1 = -\frac{\beta I_0 L_{\text{eff}}}{2\sqrt{2}(1+x^2)} \quad (3)$$

where  $k = 2\pi/\lambda$  is the wave number,  $x = z/z_0$ ,  $I_0$  the field intensity at the beam waist and  $L_{\text{eff}} = (1 - e^{-\alpha L})/\alpha$  with  $L$ , the sample length and  $\alpha$  the linear absorption coefficient.  $L_{\text{eff}}$  is the effective length of the material.  $T_R$  and  $T_I$  are the close and open transmittances measured (non-normalized quantity). For the validity of the above relations it is necessary that  $\Delta\phi_{\text{NL}} = k \cdot n_2 \cdot I \cdot L_{\text{eff}} \ll 1$  where  $\Delta\phi_{\text{NL}}$  is the nonlinear phase shift. Eq. (2) shows that normalized close transmittance is proportional to the input intensity with the proportionality factor directly dependant on the nonlinear refractive index  $n_2$ . Therefore,  $n_2$  is deduced from the slope of the experimental curve  $T_R = f(I_0)$ .

From the above analysis it is clear that the technique is very sensitive to the linearity of the sensor as well as to the precision in the determination of the sample position  $z = x \cdot z_0$ .

To eliminate the influence from these parameters, we take transmittance measurements simultaneously, in a reference sample and in the sample to be tested. Fig. 2 shows the experimental setup used for these measurements where, the scripts (r) and (t) refer to reference sample and to test sample respectively.

The experiments were performed with a amplified, mode locked Nd:YAG laser that delivers 30ps pulses at  $\lambda = 1064\text{nm}$  with a repetition rate of 10Hz. A half-wave plate placed before a Glan polarizer ( $P$ ) permits the adjustment of the total input energy. Control of the input pulse energy is achieved by means of a beam splitter ( $BS_1$ ) that sends about 4% of the beam on a silicon photodiode ( $D_c$ ) connected to a 4-channel numerical oscilloscope. A second beam splitter ( $BS_2$ ) splits the laser pulses in two parts of approximately equal energies. One pulse is sent on the sample under test (t-sub-

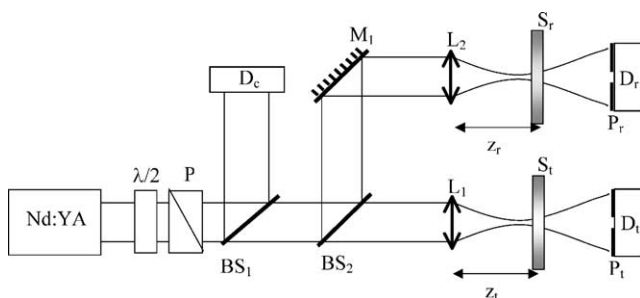


Fig. 2. Experimental setup:  $D_c$ ,  $D_r$ ,  $D_t$  are photodiodes.  $S_t$  and  $S_r$  are test and reference samples respectively.

scripted) and the other on the reference sample (r-subscripted). The two beams are then focused using lenses  $L_1$  and  $L_2$  to 40–80  $\mu\text{m}$  spots. In the far field two similar silicon photodiodes ( $D_r$  and  $D_t$ ) collect the transmitted energy through small apertures ( $P_r$  and  $P_t$ ). The positions of the two samples are fixed at about one Rayleigh length after the waist of each beam. This position is chosen because it corresponds to an extrema in the typical  $z$ -scan experiment and therefore, as it will be shown in the following, it gives measurements with higher resolution.

The reference and the test media have respectively the nonlinear refractive coefficients  $n_2^r$  and  $n_2^t$ , their effective thicknesses, respectively  $L_{\text{eff}}^r$  and  $L_{\text{eff}}^t$  and their normalized transmittances, respectively  $\Delta T_r$  and  $\Delta T_t$ . Then, taking into account Eq. (2), we can express  $\Delta T_t$  as a function of  $\Delta T_r$  with the following linear relation:

$$\Delta T_t = C \cdot \frac{L_{\text{eff}}^t n_2^t}{L_{\text{eff}}^r n_2^r} \Delta T_r \quad (4)$$

where the coefficient  $C$  is given by

$$C = \frac{I_0^t x_r (1+x_r^2)(9+x_r^2)}{I_0^r x_t (1+x_t^2)(9+x_t^2)} \quad (5)$$

and depends implicitly or explicitly on several experimental parameters (peak intensity in each branch, position of the samples, detectors response). The value of  $C$  is experimentally determined by placing in the test branch an identical to the reference sample. This calibration measurement is done once and is valid for all consecutive measurements. Once  $C$  is known, the nonlinear refractive index of the sample under test  $n_2^t$  can be calculated by Eq. (4) as a function of the nonlinear refractive index  $n_2^r$  of the reference material.

#### 4. Results and discussions

A typical absorption spectrum of the synthesized molecules measured at low concentrations and dissolved in methanol is shown in Fig. 1. This curve shows that the studied molecules have no optical losses between 532 nm and 1064 nm. However, for the study of the nonlinear properties of the materials, higher concentration is necessary and this can lead to stronger absorptions.

Measurements of the dependence of samples transmission into the total aperture on the sample coordinate along the focal waist confirm the absence of two-photon absorption at the wavelength of 1064 nm. So the linear and nonlinear absorption coefficients ( $\alpha$  and  $\beta$ ) of the sample under test can be neglected at 1064 nm and with the beam intensities that we used. This result well agrees with the recorded absorption spectra of our salts.

The measurements of the nonlinear re coefficient  $n_2^t$  of the samples are performed using the procedure described above. The nonlinear medium is made up of powdered

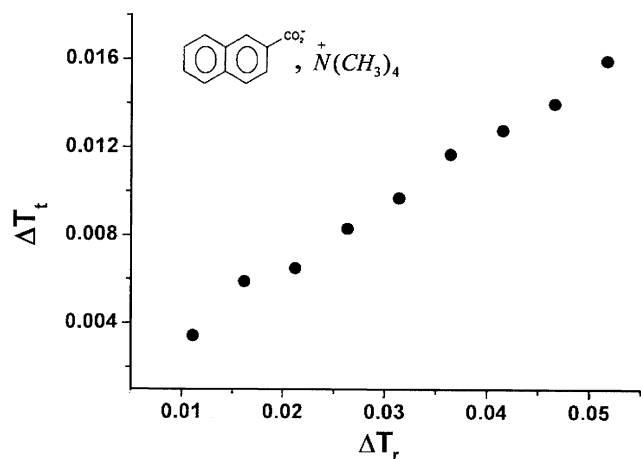


Fig. 3. Experimental plot of test sample transmittance variation  $\Delta T_t$  as a function of transmittance variation of reference sample, for molecule shown in the inset.

organic material dissolved in methanol, which display third order susceptibility at 1064 nm negligible relatively to that of the powder. We used cells of 5 mm of path length and varied the intensity (at the beam waist) from 0.7 to 4.5 GW/cm<sup>2</sup> approximately. A typical experimental curve obtained in this way is shown in Fig. 3 and represents the variation of the transmittance of the test sample versus the one of the reference sample. For all measurements presented in this paper we used as reference sample a 1 mm long cell with benzene (C<sub>6</sub>H<sub>6</sub>). Benzene was preferred to carbon disulfide (CS<sub>2</sub>) which is the most commonly used reference material for  $\chi^{(3)}$  measurements, because several experiments in our laboratory have shown that CS<sub>2</sub> presents a rather complex behavior for intensities larger than 400 MW/cm<sup>2</sup>, indicating that other nonlinear phenomena can simultaneously take place [28]. A typical experimental result is shown in Fig. 3 where the variation of transmittance of the test sample  $\Delta T_t$  is plotted as function of one of the reference sample  $\Delta T_r$ . The linear dependency between  $\Delta T_t$  and  $\Delta T_r$  in this figure indicates that the measured nonlinearities are predominantly refractive and non-resonant. The nonlinear refractive index of the samples is expressed relatively to that of benzene. From the open aperture measurements it was well verified that none of the samples presented nonlinear absorption in the laser wavelength and in the range of work intensities. The absence of two-photon absorption was expected as shown by the absorption spectrum of the materials (Fig. 1).

As shown in Fig. 4, the third order susceptibility ( $\chi^{(3)}$ ) measured is proportional to concentration  $C_{\text{solute}}$  for small values of  $C$ . This is in agreement with the theoretical predictions for a dilute medium

$$\chi^{(3)} \approx F^4(C_{\text{solute}}\gamma_{\text{solute}}) + \chi_{\text{solvent}}^{(3)} \quad (6)$$

where  $F = (n^2 + 2)/3$  is the Lorentz field factor correction,  $n$  the refractive index of the medium and  $\gamma_{\text{solute}}$  is

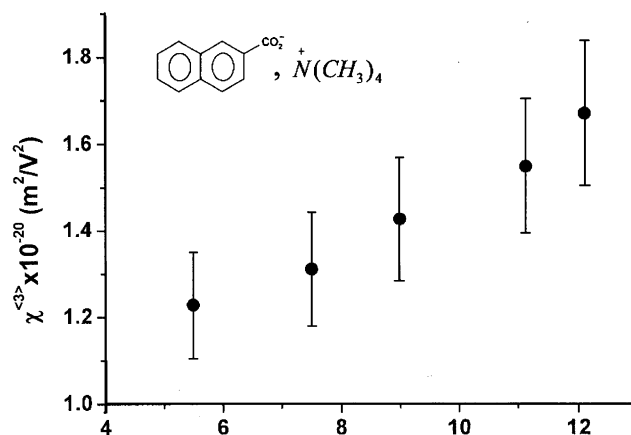


Fig. 4.  $\chi^{(3)}$  value versus concentration curve for the molecule.

the molecular hyperpolarizability of the individual molecule of the material. The nonlinear susceptibility of the solvent (methanol) being very small here, can be neglected. One can thus write

$$\gamma_{\text{solute}} = \frac{\chi_{\text{solute}}^{(3)}}{F^4 N} \quad (7)$$

where  $N = N_A C/M$  is the number molecules of the solution per unity of volume,  $N_A$  is the Avogadro number,  $C$  is the concentration and  $M$  the molecular mass of the compound.

Table 1 summarizes the obtained results for all tested materials. Using Eq. (7), in the third column of this table, we give the calculated polarizability  $\gamma_{\text{solute}}$  for the tested materials. We remark that at the molecular level, these new materials present a remarkably large nonlinearity, five and six orders of magnitude larger compared to CS<sub>2</sub> and CHCl<sub>3</sub> respectively.

## 5. Conclusion

The investigation of nonlinear optical properties of new salts of carboxylate anions with chiral amines and ammonium cations at 1.06 μm wavelength has allowed us to find the values of third order susceptibility in samples of interest. Using a new alternative to the classical z-scan technique with 30 ps laser pulses, we have shown that these materials have fast responses, large hyperpolarizabilities  $\gamma$  which can vary between  $1.2 \times 10^{-49}$  SI and  $4.4 \times 10^{-48}$  SI. These values are higher than those usually found in standard organic materials. The investigated materials have the important advantage of very weak linear and two-photon absorption at wavelength of the near IR, enabling application in various optical systems such as switching, multiplexing and demultiplexing. These results emphasize the interest for nonlinear optical properties of ionic compounds based upon large polarizable anions.

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