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# The influence of pH in nonresonant third-order nonlinearities of amino acid solutions

***J. J. Rodrigues Jr., N. M. Barbosa Neto, S. C. Zilio, D. T. Balogh, L. Misoguti, C. R. Mendonça***

**Instituto de Física de São Carlos - USP**

*Joatan@if.sc.usp.br*

## Abstract

*We report on the use of the Z-scan technique with femtosecond pulses at 775 nm to investigate the electronic charge delocalization in L-arginine, L-proline and L-serine amino acids. We have observed a variation in the nonresonant nonlinear transmittance with the pH, which reflects the variation in the relative concentration of the cationic and anionic forms and, consequently, the electronic charge delocalization A good correspondence between the measured nonlinear transmittance variation and the titration curve was observed for the three amino acid samples, in the pH range studied. The* $n_2$ *values measured range from* $10^{-17}$ *to* $10^{-16}$ $cm^2/W$ *for pH varying from about 2 to 9.2.*

# Introduction

Organic materials have been extensively studied as candidates for all-optical devices because of their interesting optical properties allied to the flexibility of molecular engineering by chemical manipulation. In particular, some effort has been directed to understand and developing second order nonlinear optical properties of amino acids crystals[1,2], which generally exibit efficient harmonic generation and present good environmental. For instance, L-arginine phosphatated (LAP) have shown favorable nonlinear properties as a second harmonic generator (SHG) [2]. Recently, the third-order optical nonlinearities in several amino acids water solutions were measured using the Z-scan technique with femtosecond laser pulses [3]. The origin of the refractive nonlinearity was shown to be predominantly electronic, with the nonlinear refractive index $n_2$ ranging from $10^{-17}$ to $10^{-16}$ $cm^2/W$. Moreover, these results indicated a relation between the amino acids molecular charge (polar or apolar) and the third-order nonlinear optical response (second hyperpolarizability), in agreement with theoretical quantum chemical calculations. However, the experiments reported in [3] were performed with the solution in a fixed pH.

In this work we report the correlation between the nonresonant Z-scan measurements and the solution pH, for three different amino acid aqueous solutions. By changing the pH of these solutions, a variation in the concentration of cationic and anionic amino acid forms is observed. Since the charge distribution has a direct effect in the molecular hiperpolarizability, the third-order nonlinear optical process is sensitive to the pH variation. In this way, using the Z-scan technique with femtosecond pulses at 775 nm we investigate the correlation between the nonresonant third-order nonlinear process and the charge distribution in amino acids belonging to the three main classes, (i) non-polar, (ii) uncharged polar and (iii) charged polar. Figure 1 shows the molecular structure predominating at pH=7, for the molecules studied in this work, namely L-proline (non-polar), L-serine (uncharged polar) and L-arginine (charged polar).

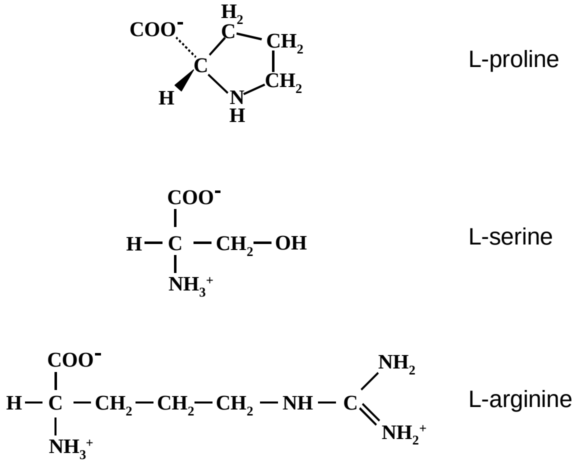

**Figure 1:** Predominating molecular structure at pH = 7.0 for L-poline, L-serine and L-arginine.

## Experimental Setup

The L-arginine, L-proline and L-serine solutions, in different pH, were prepared at room temperature (22 $^{0}$C) with the addition of proper amounts of standard HCl or NaOH and filling with water to a fixed volume in a volumetric flask. Blank solutions (reference) were prepared in the same way, without the addition of the amino acids. Crystallization was avoided by keeping all samples in concentrations below their solubility limit. The “half” titration curves (pH versus volume of acid/base added) were obtained by measuring the pH values of the final amino acid solutions with a pH-meter. The absorption spectra in the UV-Vis region were obtained with a Cary 17-A spectrophotometer. All samples studied in this work present an absorption peak around 200 nm, being completely transparent in the visible and near infrared regions [4] as it is well known for non-aromatic amino acids. Therefore, nonlinear optical measurements (performed at 775 nm), whose description is given subsequently, were carried out under non-resonant excitation.

The Z-scan is a well knows technique that allows measuring precisely the magnitude and the signal of refractive and absorptive nonlinearities [5]. In our Z-scan experiment we have used laser pulses delivered by a commercial Ti:sapphire chirped pulse amplified system CPA-2001 from Clark-MXR Inc., operating at 775 nm at a 1 kHz repetition rate. The typical pulse energy employed in our investigation was about 0.25 μJ, and the pulse duration 190 fs. The beam waist size ($\omega_0$ = 13 μm) and pulse irradiance were determined by performing Z-scan measurements in fused silica (1.2 mm) [6]. Z-scan measurements were carried out with the sample placed in a quartz cuvette (optical path: 2 mm).

## Results and Discussions

The figure 2 shows the $\Delta T_{pv}$ variation curve obtained for the L-proline (a), L-serine (b) and L-arginine (c) samples as a function of the solution pH. As can be seen, the Z-scan measurement (circles) presents a symmetric curve around a pH value. For comparison, the “half” titration curve (solid for HCl and dashed lines for NaOH additions) were also plotted, but with the y axes exchanged in order to match the $\Delta T_{pv}$ variation curve. The Z-scan measurement follows the “half” titration curves, once the results of both techniques depend on the molecular structure. The different amplitudes observed for the $\Delta T_{pv}$ variation in this figure are related to distinct final concentration employed due to the different solubility of the amino acids.

According to the results presented in Fig. 2, as the nonlinear process amplitude $\Delta T_{pv}$ is proportional to $n_2$, one can conclude that the pH variation that induced protonation or deprotonation alters the magnitude of the induced molecule dipole moment. The symmetry observed in the nonlinear transmittance as function of the pH, reflects the second hyper-polarizability dependence on the dipole moment amplitude, being independent of which group (carboxylate or protonated amino) is more or less charged.

It is also clear for the experimental results presented in Fig. 2 that each sample exhibits a symmetrical curve around a different pH value. For instance, L-serine (curve b), is symmetrical around pH = 6.0. This pH value corresponds to the isoelectric point (pI), defined as the mean value between $pK_a$ and $pK_b$, when the solution presents only two equivalence points. This value found through the Z-scan technique for the isoelectronic point (6.0) is in very good agreement with the value found in the literature [7], which is 5.7. Furthermore, the isoelectronic point found for L-proline through the Z-scan was 6.5. Again, this values is in very good agreement with that found in the literature, 6.3 [7]. For L-arginine, a basic amino acid, there exist three equivalence points, as a result of the second base function presented in this molecule in addition to the amine base present in all amino acids. In this way, for L-arginine we just determine the intermediate point between $pK_a$ and $pK_{b1}$ (relative to the first base function) and not pI, which is 10.76. The mean value between $pK_a$ and $pK_{b1}$ measured through the Z-scan technique was 5.5, which is in very good agreement with that found in the literature (5.4) [7]. The experimental results for $\Delta T_{pv}$ correspond to $n_2$ ranging from $10^{-17}$ to $10^{-16}$ cm$^2$/W, respectively, in agreement with [3].

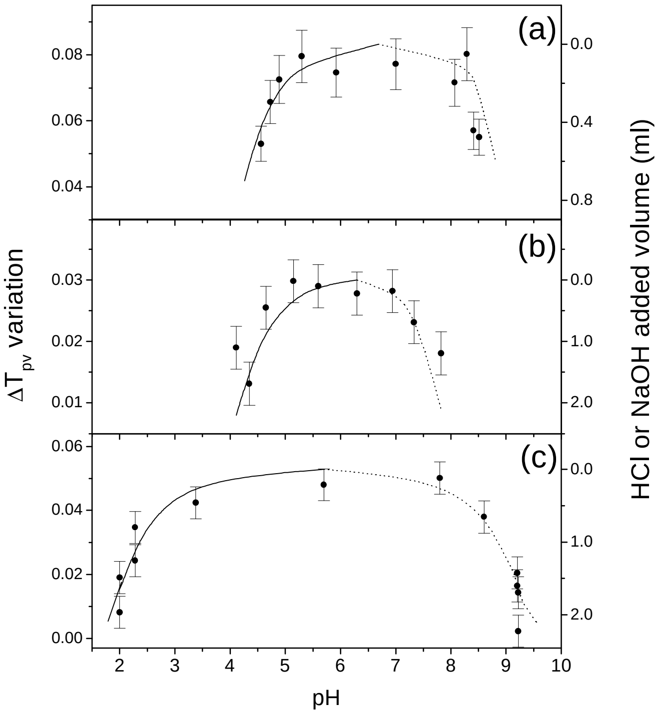

**Figure 2:** $\Delta T_{pv}$ variation as a function of the amino acid solution pH (circles) and “half” titration curves (solid and dashed lines) for the samples of (a) L-proline, (b) L-serine and (c) L-arginine.

## Conclusions

The present investigation shows for the first time, at our knowledgement, that it is possible to observe a correlation between the molecular charge delocalization and the nonresonant nonlinear process in amino acids using the Z-scan technique. As the nonlinear transmittance follows the amino acid solution titration curve, the Z-scan technique could be used to determine the titration curve features, and investigate the charge delocalization in this type of compound.

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