Third order nonlinearities in several amino acid solutions

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Abstract

We report an investigation of third-order optical nonlinearities in several amino acid solutions using the Z-scan technique with femtosecond laser pulses at 775 nm. The nonlinear refractive index n_2 in these aqueous solutions has been determined to be in the range from 10^{-17} to 10^{-16} cm^2/W (γ raging from $0.9x10^{-36}$ to $3.3x10^{-36}$ esu). The experimental second molecular hyperpolarizabilities obtained for each amino acid are in good agreement with semi-empirical AM1 calculations.

Introduction

Organic materials are promising systems for photonics due to their large optical nonlinearities and fast response [1,2]. Accordingly, second and third order nonlinear optical properties of various organic materials have been extensively investigated through many experimental and theoretical methods [3,4]. Organic crystals have attracted a great deal of attention mainly for practical applications in manufacturing waveguides, filters and others devices. Among organic crystals, amino acids such as L-asparagine, L-arginine [7] and L-alanine [8] have been studied, due to their potential use as SHG and OPA [5,6], for instance.

The present work reports on the third-order optical nonlinearities in several amino acids water solutions using the Z-scan technique with femtosecond laser pulses at 775 nm. Z-scan measurements were carried out in five different amino acids, belonging to three different groups; i) apolar: L-alanine, L-proline ii) charged polar: L-arginine iii) uncharged polar: L-threonine, L-serine. The nonlinear refractive index n_2 in these amino acids aqueous solutions have been determined to be in the range from 10^{-17} to 10^{-16} cm^2/W. The main interest here is to characterize these materials in order to help the understanding of the nonlinear properties and guide further works with other amino acids. In order to accomplish this task we compare the results for these five systems and their theoretical second hyperpolarizability (γ), obtained through quantum chemical calculations (AM1 method).

Experimental Setup

Amino acid solutions were prepared at room temperature (22 ^{0}C) with H_2O in a pH of 6.5, in a concentration below the solubility limit to avoid crystallization. With this pH, all amino acids studied are in their zwitterionic form, meaning that their carboxylate (COO^-) and amine ($NH3^+$) groups are charged [7]. All Z-scan measurements were carried out with the sample placed in a quartz cuvette (optical path: 2 mm).

In our Z-scan experiment were used laser pulses at 775 nm delivered by a commercial Ti:sapphire chirped pulse amplified (CPA) system CPA-2001 from Clark-MXR Inc., operating at a 1 kHz repetition rate. The typical pulse energy employed in our investigation was about 0.25 μJ. The FWHM pulse duration was 190 fs, and the spatial profile of the laser beam approximately Gaussian. The beam waist size (ω_0 = 13 μm) and pulse irradiance were determined by performing Z-scan measurements in fused silica (1.2 mm) [8].

Since the intensities levels achieved with femtosecond pulses are extremely high, even the quartz cuvette contribution to the nonlinearity has to be considered. Thus, the thin sample standard [9,10], is not applicable to our Z-scan experiments, because the combination of the sample and quartz thickness is greater than the laser beam diffraction length. We have modified the Hermann and MacDuff [11] method for Z-scan of thick samples to include the quartz cuvette windows before and after the sample of interest and fitted it to the experimental data. The water contribution to our measurement was eliminated by subtracting the n_2 values the amino acid aqueous solution and pure water. In this way, by doing that we were able to infer about the nonlinear refractive index just due to the amino acids.

Results and Discussions

All compounds used in this work present an absorption peak around 200 nm, being completely transparent in the visible and near infrared regions. [12] Accordingly, nonlinear optical measurements were made under non-resonant excitation. Figure 1 shows the Z-scan measurement for the L-proline solution and water. This Z-scan signature indicates a self focusing (positive nonlinearity). The n_2 values were determined with the procedure previously mentioned. The solid lines in this figure represent theoretical fittings obtained with the Hermann and McDuff [11] modified model, with the parameters $n_2 = 1.2 \times 10^{-16}$ cm^2/W for the water sample and $n_2 = 2.0 \times 10^{-16}$ cm^2/W for the amino acid solution. Similar Z-scan measurements were carried out for the other amino acid solutions in order to determine their nonlinear refractive index. The n_2 values measured range from 10^{-17} to 10^{-16} cm^2/W, and no two-photon absorption process or white light generation was observed.

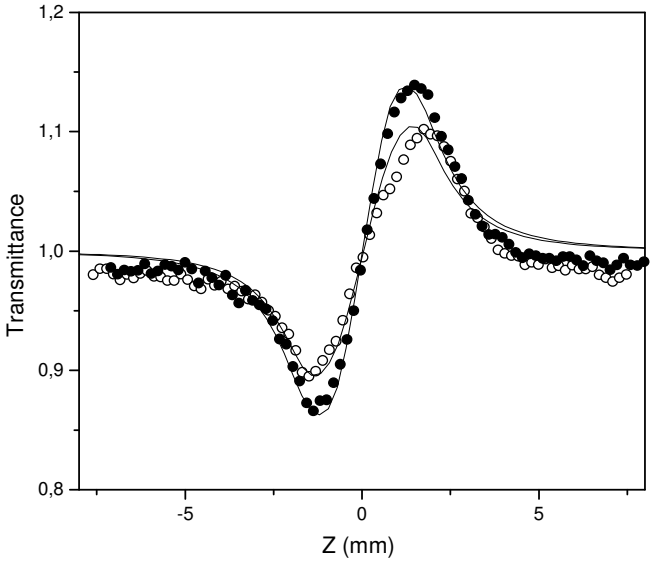

Figure 1 – Z-scan signature for the L-proline aqueous solution (close circles) and water (open circles) performed with 150 fs pulses at 775 nm and an intensity of 200 GW/cm^2. The solid lines represent theoretical fittings obtained with the expression and parameters given in the text.

The values obtained for the second hyperpolarizability γ indicate the relation between the molecular charge (polar or apolar) and the third-order nonlinear optical response. As can be seen in figure 1. The origin of the refractive nonlinearity is predominantly electronic, once we performed the experiment under nonresonant condition (linear and nonlinear absorption negligible).

To get a better understanding of the microscopic origin of the nonlinearity in amino acids, we compare the experimentally determined values of γ with those resulting from a quantum chemical calculation obtained with the MOPAC 6.0 program [13,14] (semi-empirical Austin Model 1 – AM1 method). Figure 2 shows a general agreement between the trends of experimental and theoretical γ values. The differences observed are probably related to some incompleteness of the semi-empirical calculation, which was performed in gas-phase and for the molecules with extended conformations.

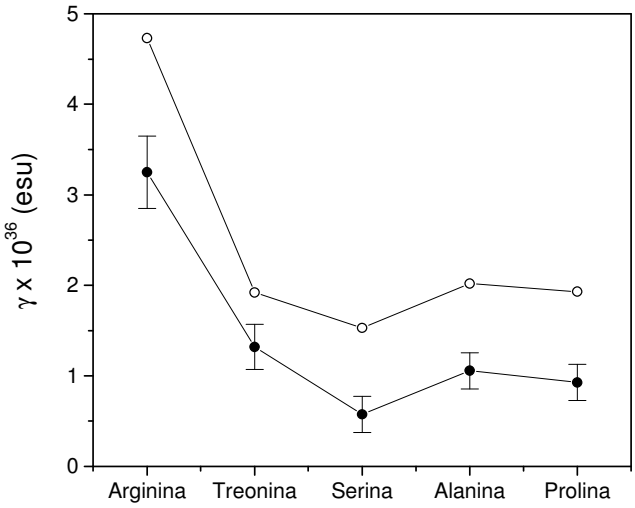

Figure 2 – Experimental (closed circles) and theoretical AM1 (open circles) values of the second order molecular hyperpolarizability, γ, for the five amino acids studied.

Conclusion

We have carried out an investigation of third-order optical nonlinearity in several amino acid/water solutions using the Z-scan technique with 775 nm femtosecond laser pulses. The nonlinear refraction index n_2 range from 10^{-17} to 10^{-16} cm^2/W, and no two-photon absorption process has been observed. This results indicates that the third order nonlinear process in amino acids is not a main limitation for second order nonlinearity based devices. It was found that the experimental results and theoretical AM1 quantum chemical calculation of the second hiperpolarizability for the amino acids studied here are in very good agreement, considering the simplicity of the model.

Acknwoledgments

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