Picosecond z-scan measurements of the two-photon absorption in beta-carotene solution over the 590-790 nm wavelength range

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ABSTRACT

The two-photon absorption (TPA) properties of β-carotene (beta-carotene) in chloroform solution were investigated over the 590-790 nm wavelength range. The TPA was characterized using the open-aperture z-scan technique with picosecond pulses provided by a widely traveling-wave optical parametric amplifier (OPA) pumped with a Ti:sapphire laser amplifier. We found the 0.2-1 cm/GW values of two photon absorption coefficient in the 725-790 nm wavelength region. At shorter wavelengths, a dramatic increase in the two-photon absorption around 600 nm was observed. The observed two photon absorption dependence on the excitation wavelength can be explained by the onset of strong excitation from the ground state $1A_g$ to the higher lying two-photon allowed m_2A_g band centered around 310 nm (~4 eV).

Keywords: Optical nonlinearities in organic materials; Nonlinear spectroscopy; Two-photon absorption

1. INTRODUCTION

One-dimensional π-conjugated organic molecules, such as β-carotene (see Fig. 1), are characterized by large optical nonlinearities due to their highly delocalized π-electronic cloud [1-4] and therefore are very attractive for a wide range of applications in the field of optical technology. Though third-order nonlinearities of β-carotene were extensively studied both theoretically and experimentally via third-harmonic generation [1-4], little is known about its two-photon absorption (TPA) properties. For example, strong two-photon absorbers are important in applications such as optical signal limiting [5], adaptive ultrashort pulse shaping [6] and nonlinear microscopy [7]. Knowledge about the two-photon absorption properties of carotenoids is an important issue in the multiphoton excitation microscopic imaging of carotenoid containing biological samples, since energy deposition in the sample via TPA process can result in sample degradation and photobleaching. Careful characterization of the TPA of carotenoids is also important in the

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investigations of excitation energy transfer processes in the photosynthetic light-harvesting antenna, where optically forbidden transitions can be accessed via two-photon excitation processes [8].

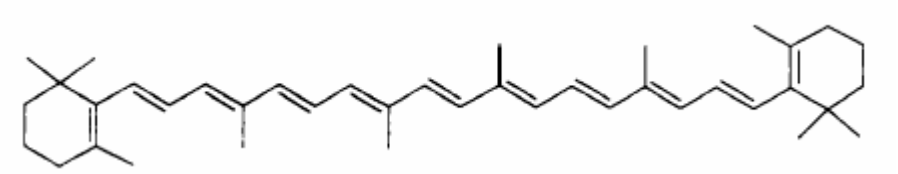

Fig. 1. Molecular structure of the β-carotene molecule.

Here we report systematic broadband characterization of the TPA properties of β-carotene in chloroform solution over the 590-790 nm wavelength range.

2. EXPERIMENTAL TECHNIQUE

To characterize the TPA properties of β-carotene solution we used a standard configuration of the well-known single-beam z-scan technique [9], which can accurately measure the magnitude of both nonlinear absorption and the nonlinear refractive index coefficient. The z-scan measurement involves monitoring of the transmission through an open (closed) aperture, placed in the far field while scanning a thin sample through the focal point of a focused laser beam. The advantage of the z-scan technique is that the relative change in the transmission through the open (closed) aperture is directly proportional to the magnitude of the nonlinear absorption (nonlinear refractive index).

For our measurements we used the spatially filtered output of an optical parametric amplifier (TOPAS, Light Conversion Ltd.) pumped at 800 nm by a picosecond regenerative, multipass chirped-pulse Ti:sapphire amplifier (TITAN, Quantronix) operating at a 1 kHz repetition rate (see Fig. 2).

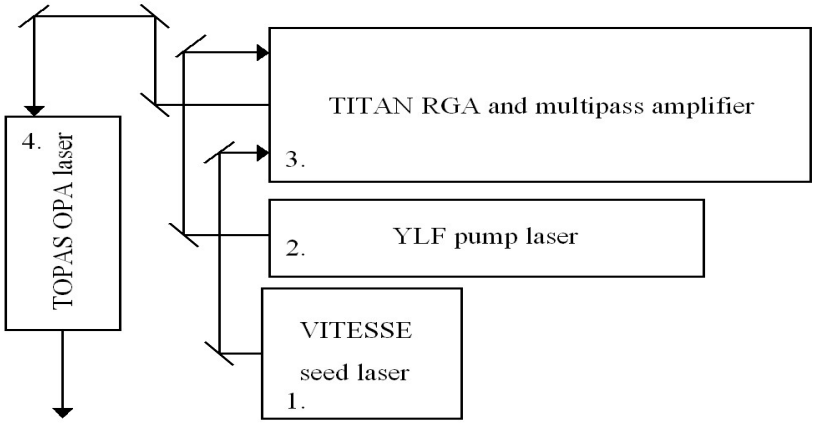

Fig. 2. Laser system - femtosecond seed laser 1, frequency doubled pump laser 2, Ti:S regenerative and multipass amplifier 3, optical parametric oscillator 4.

The output of the optical parametric amplifier was tunable in the 590-790 nm wavelength region with pulse energies in excess of 1 μJ. The pulse duration in this tuning range was around 1 ps. A schematic layout of the

experimental z-scan setup is shown in Fig. 3. The output of the OPA was first spectrally filtered using a Glan polarizer, attenuated with half-waveplate and a second polarizer, and spatially filtered. Using a 150 mm focal length lens the output of the OPA was focused to approximately a 25 μm diameter spot size.

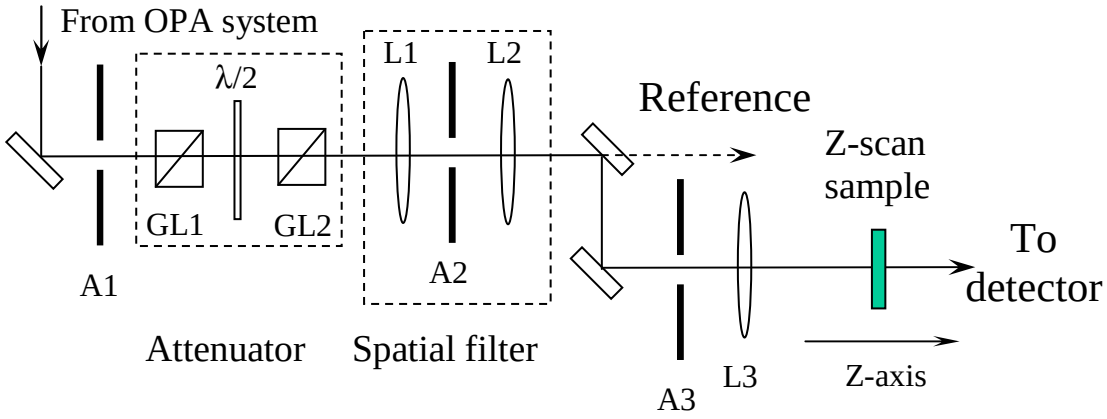

Fig. 3. Layout of the z-scan experiment - apertures A, lenses L, Glan polarizers GL.

Depending on the wavelength, pulses with 1-24 nJ pulse energies were used resulting in the maximum on-axis light intensities in the range of 0.5-12 GW/cm^2, respectively. For detection (reference and open aperture) we used calibrated power meters (Ophir Optronics Ltd., LaserStar).

The sample was mounted on a precision translation stage (Newport, MTM200PP1). The translation stage along with the data acquisition system was computer controlled using a LabView interface program. To reduce the level of noise in the measurements caused by laser power fluctuations the recorded signal was divided by a signal from a reference arm detector (see Fig. 3).

A 1 mm-thick BK7 glass cuvette with the solution of β-carotene in chloroform (1.19 mg/ml) was used as a sample. To avoid sample degradation the experiments were carried out in dark room conditions.

Knife-edge measurements confirmed that the beam profile is circular in shape and close to diffraction limited with $M^2 < 1.1$. A typical transverse beam intensity pattern taken with an imaging camera is shown in Fig. 4.

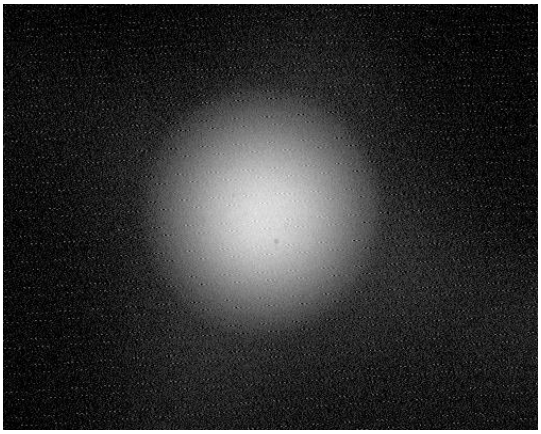

Fig. 4. Transverse beam intensity pattern.

3. DATA ANALYSIS

Open-aperture z-scan traces recorded at 720 and 610 nm are shown in Fig. 5, along with theoretical fits to data (solid curves), as typical examples. Similar results were obtained for all wavelengths, and the same procedure was used to analyze the data. The magnitude of the two-photon absorption coefficient β can be determined from the depth of a dip in the open-aperture z-scan trace that is directly related to the β value.

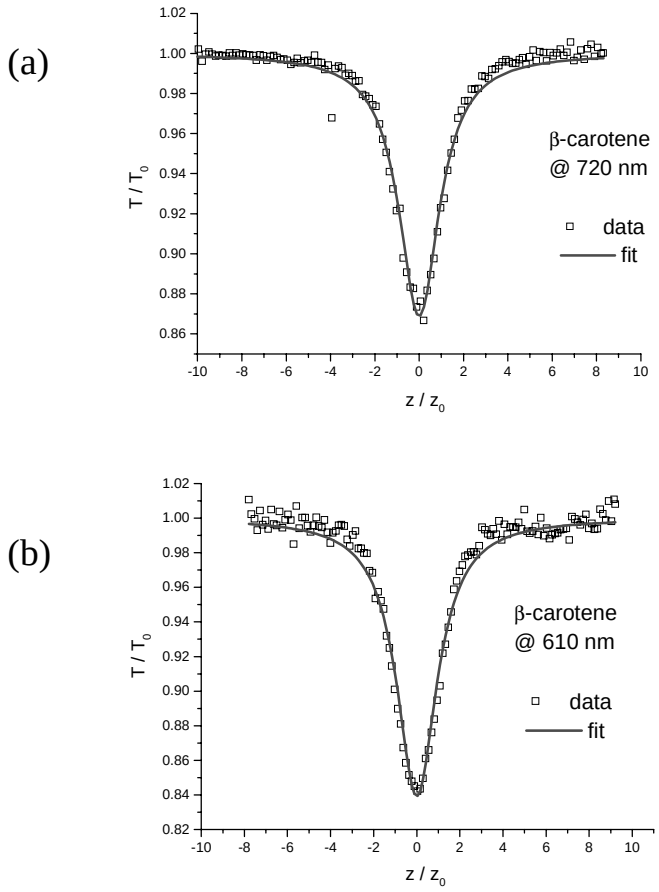

Fig. 5. Examples of the open-aperture z-scan traces.

TPA coefficients were calculated with a high degree of accuracy from the best fits to the corresponding z-scan data (see Fig. 5) using the expressions derived in [9]. These calculations were performed assuming a quasi-monochromatic optical field so that the slowly varying envelope approximation (SVEA), a Gaussian beam under the condition for the paraxial approximation and a sample with cubic nonlinearity can be applied. For such material, the index of refraction and the absorption coefficient are expressed in terms of the nonlinear index n_2 and the two-photon absorption coefficient β, respectively, through the equations

$$n = n_0 + n_2 I \tag{1}$$

and

$$\alpha = \alpha_0 + \beta I \,, \tag{2}$$

where n_0 is the linear index of refraction, α_0 is the linear absorption coefficient and I denotes the irradiance of the laser beam within the sample. The medium is regarded as "thin" when using a beam whose changes in the diameter within the sample due to either diffraction or nonlinear refraction can be neglected. For a sample with length L, this implies that $L<<n_0z_0$ (linear diffraction) and $L<<n_0z_0/\Delta\Phi_0$ (nonlinear refraction), where z_0 is the Rayleigh range of the Gaussian beam (~1.6 mm in our case), $\Delta\Phi_0 = kn_2I_0L_{\text{eff}}$ is the peak nonlinear phase distortion, $k=2\pi/\lambda$ is the wave vector, I_0 is the on-axis and in-sample peak irradiance at focus, and $L_{\text{eff}} = (1-e^{-\alpha_0 L})/\alpha_0$ is the effective sample length.

The normalized z-scan transmittance $T(z)$ can be expressed as the ratio of the transmitted power through the aperture divided by the transmitted power though the aperture in the absence of any nonlinearity, or

$$T(z) = \frac{\int_{-\infty}^{+\infty}\int_{0}^{r_\alpha} I_\alpha(z,r,t,\Delta\Phi_0,q_0)\,r\,dr\,dt}{\int_{-\infty}^{+\infty}\int_{0}^{r_\alpha} I_\alpha(z,r,t,\Delta\Phi_0=0,q_0=0)\,r\,dr\,dt}, \tag{3}$$

where $q_0 = \beta I_0 L_{\text{eff}}$ is a parameter that denotes the strength of the two-photon absorption, r_α is the aperture radius, and $I_\alpha = \frac{1}{2}\varepsilon_0 c\left|E_\alpha\right|^2$ is the intensity of the electric field E_α on the aperture plane.

For a temporally Gaussian pulse and for $|q_0|>1$ the open aperture z-scan transmittance curves were calculated by means of the integral [9]

$$T(z) = \frac{1}{\sqrt{\pi}q_0(z)}\int_{-\infty}^{+\infty}\ln\left(1+q_0(z)\exp(-\tau^2)\right)d\tau, \tag{4}$$

where $q_0(z)=q_0/(1+z^2/z_0^2)$. On the other hand, for $|q_0|<1$ we used the simplified expression

$$T(z) = \sum_{m=0}^{\infty}\frac{(-q_0)^m}{(m+1)^{3/2}}, \tag{5}$$

which is also in a form more appropriate for numerical evaluation. Both expressions were used because we performed a large number of z-scan experiments, using different wavelengths and input intensities before we were able to derive reliable experimental results and conclusions regarding the origin of the nonlinear phenomena observed. For example, we have verified experimentally that the resulting parameters are intensity independent, i.e. that the observed effects were not due to higher order nonlinearities (see Fig. 6). It was also verified that an open-aperture z-scan trace with neat $CHCl_3$ liquid does not contribute to the observed TPA signal.

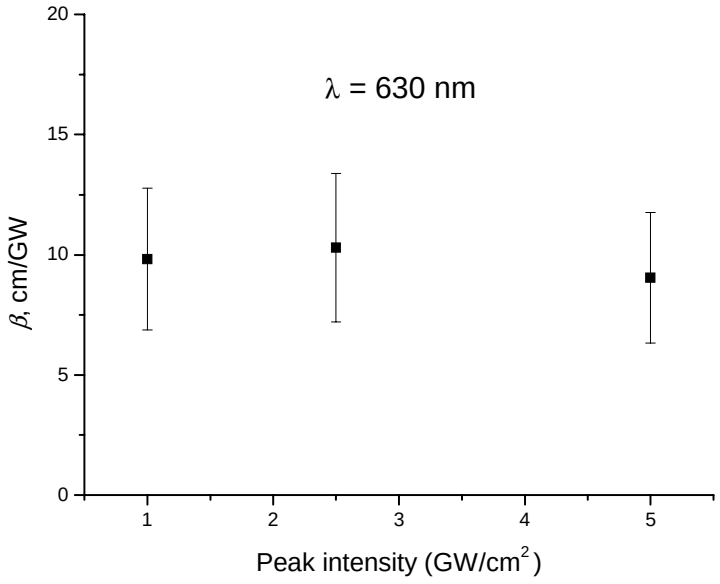

Fig. 6. Intensity dependence of the TPA coefficient. Error bars are set at 30%.

Including all error sources, the uncertainty in the measured values was estimated to be ± 25–30% depending on wavelength, which is typical for experimental errors in z-scan measurements [9]. The main contributions to the uncertainty arose from the power, the pulse width, and the beam waist radius measurements, laser power fluctuations and uncertainty in the fitting procedure.

4. RESULTS AND DISCUSSION

The experimental results are summarized in Fig. 7. Linear absorption spectrum is also shown as a solid curve. Characteristic strong linear absorption in the 400-500 nm region reduced the signal below the sensitivity level of detection and precluded to obtain full shape of the absorption peak around 464 nm [1-4]. The shaded area in Fig. 7 represents the wavelength region corresponding to twice the photon energy of the laser radiation used in the TPA measurements.

We have found that the TPA in the 725-790 nm region is ~0.2-1 cm/GW. At shorter wavelengths it grows with a dramatic increase in the TPA values around 600 nm. The observed dependence can be explained by the onset of strong absorption from the ground state $1A_g$ into the higher lying two-photon allowed m_2A_g band centered around 310 nm (~4 eV) [3]. The energy diagram for β-carotene with corresponding two-photon transition is schematically shown in Fig. 8. Linear absorption measurements before, during and after the experiments showed no degradation of the sample.

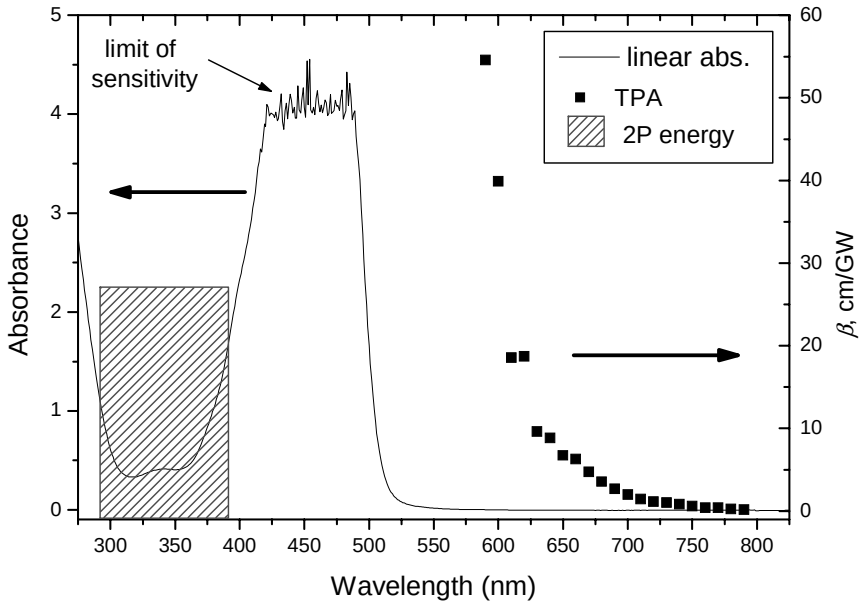

Fig. 7. Summary of the two-photon absorption measurements.

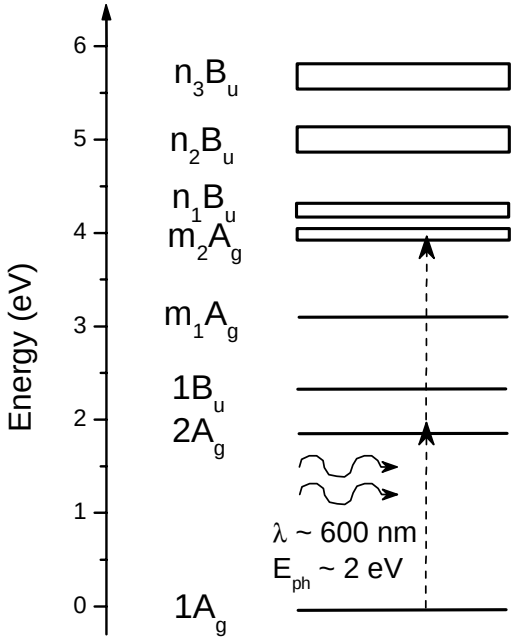

Fig. 8. Energy level diagram for β-carotene. After [3].

CONCLUSIONS AND OUTLOOK

In conclusion, we have characterized the two-photon absorption properties of beta-carotene solution in chloroform over the 590-790 nm wavelength range using an open-aperture z-scan technique. We have found that the TPA in the 725-790 nm region is ~0.2-1 cm/GW. At shorter wavelengths it grows with a dramatic increase in the TPA values around 600 nm. Strong two-photon absorption around 600 nm and can be attributed to the allowed two-photon transitions from the ground state $1A_g$ into the m_2A_g band.

Future experiments will include investigations of third-order susceptibility $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of carotenoids via third harmonic generation technique in the 700-1100 nm range.

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REFERENCES

[1] J. B. van Beek and A. C. Albrecht, "Third-harmonic generation from all-trans β-carotene in liquid solution," Chem. Phys. Lett. **187**, 269-276 (1991).

[2] S. Aramaki, W. Torruellas, R. Zanoni and G. I. Stegeman, "Tunable third harmonic generation of trans-β-carotene," Opt. Commun. **85**, 527-535 (1991).

[3] D. Beljonne, J. Cornil, Z, Shuai, J. L. Bredas, F. Rohlfing, D. D. C. Bradley, W. E. Torruellas, V. Ricci, and G. I. Stegeman, "General model for the dispersion of the third-order optical nonlinearities in conjugated systems: Application to the all-trans β-carotene molecule," Phys. Rev. B **55**, 1505-1516 (1997).

[4] S. R. Marder, W. E. Torruellas, M. Blanchard-Desce, V. Ricci, G. I. Stegeman, S. Gilmour, J.-L. Bredas, J. Li, G. U. Bublitz, S. G. Boxer, "Large molecular third-order optical nonlinearities in polarized carotenoids", Science **276**, 1233-1236 (1997).

[5] E. W. Van Stryland, Y. Y. Wu, D. J. Hagan, M. J. Soileau, and K. Mansour, "Optical limiting with semiconductors," J. Opt. Soc. Am. B **5**, 1980-1988 (1988).

[6] U. Siegner, M. Haiml, J. Kunde, U. Keller, "Adaptive pulse compression by two-photon absorption in semiconductors," Opt. Lett. 27, 315-317 (2002).

[7] J. Squier, M. Muller, "High resolution nonlinear microscopy: A review of sources and methods for achieving optimal imaging," Rev. Sci. Inst. **72**, 2855-2867 (2001).

[8] P. J. Walla, J. Yom, B. P. Krueger, and Graham R. Fleming, "Two-photon excitation spectrum of light-harvesting complex II and fluorescence up-conversion after one- and two-photon excitation of the carotenoids," J. Phys. Chem. B **104**, 4799-4806 (2000).

[9] M. Sheik-Bahae, A. A. Said, T.-H. Wei, D. J. Hagan, E. W. van Stryland, "Sensitive measurement of optical nonlinearities using a single beam," IEEE J. Quantum Electron. **26**, 760-769 (1990).