



Investigation of the Degenerate Two-Photon Absorption Cross-Section in all-trans Retinal: Nonlinear Spectrum and Molecular Structure

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Abstract – Retinal is a chromophore of foremost relevance for potential applications in bio-photonics devices. Here, we study the degenerate two-photon absorption spectrum of all-trans retinal in ethanol. We observed two peaks; one associated to the two-photon dipolar contribution to a higher energy state, which contributes to the monotonic increase of the nonlinearity below 600 nm. The other one is a two-photon transition to a lower excited-singlet state (¹Ag⁻). We modeled the two-photon absorption spectrum using a sum-over-states model. Using Density Functional theoretical calculations we show that due the presence of the β -ionone ring there is a break of planarity of the molecule which decreases the nonlinear effect.

The all-trans retinal is a polyenic chromophore of major relevance in transduction process in nervous impulses. In the last few decades, it was exhaustingly studied for applications in optoelectronic devices due its ultrafast isomerization dynamics in bacteriorhodopsin [1,2]. Previous publications using nondegenerate two-photon spectroscopy [3] obtained the low-lying excited singlet states of all-trans retinal in different solvents. However, so far there is not a consensus on the electronic states involved in one- and two-photon transitions. Moreover, spectroscopic parameters of excited states involved in these transitions such as, transition dipole moment, damping constant and oscillator strength still remain unclear. To better understand electronic states of all-trans retinal under femtosecond-laser excitation, it is necessary to characterize its nonlinear absorption behavior. In this way, using the open aperture Z-scan technique we investigated the degenerate two-photon absorption cross-section as a function of excitation wavelength.

The one-photon and degenerate two-photon absorption spectra of all-trans retinal in ethanol are illustrated in Fig. 1a. The linear absorption spectrum (dash line) correspond to the $\pi\pi^*$ transitions (¹Bu⁺), with absorption maxima around 382 nm. The 2PA spectrum (circles) peaks at approximately twice the wavelength (790 nm) of the one-photon absorption band, in agreement with others results found in the literature [3]. The solid line in Fig. 1a was obtained by fitting the experimental data using the sum-over-states approach, considering a three- energy-level diagram [4]. We associated the 2PA peak (790 nm) with a two-photon transition to the ¹Ag state, while a two-photon transition to a higher energy state (S₃) contributes to the observed nonlinear absorption monotonic increase below 600 nm.

To explain the small two-photon absorption cross-section values observed, we determined the molecular geometry and the frontier molecular orbitals of all-trans retinal. Figure 2 shows the equilibrium molecular geometry of all-trans retinal obtained via DFT calculations. Due to the presence of the β -ionone ring there is a break of planarity of the molecule, which decreases the nonlinear effect. At molecular level, this break can be associated with the intramolecular steric repulsion between the hydrogen of the ring and the polyenic chain. The lowest unoccupied and highest occupied molecular orbitals, shown in Fig. 2b, indicate that most of the charge density is concentrate on the polyenic chain, corroborating the small 2PA cross-section of the chromophore at room temperature.

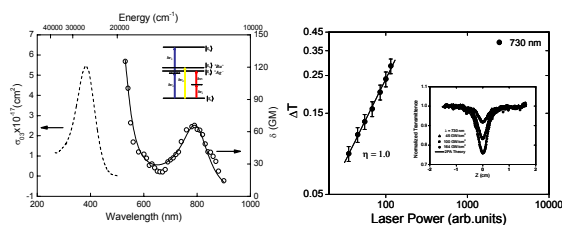


Figure 1: (a) One- and two-photon absorption spectra of ATR. (b) Plots of normalized transmittance variation (ΔT) vs. laser power at a wavelength 730 nm.

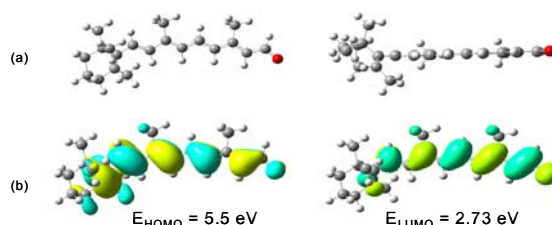


Figure 2: (a) Equilibrium molecular geometry and (b) representation of the molecular orbitals of HOMO and LUMO of all-trans retinal HOMO and LUMO of all-trans retinal.

References

- [1] N. Hampp, Chem. Rev., 100 (2000).
- [2] G. Zgrablic, K. V. Tchovsky, M. Kindermann, S. Haacke, M. Chergui, Biophysical Journal, 88 (2005).
- [3] S. Yamaguchi, T. Tahara, Chemical Physics Letters, 276 (2003).
- [4] K. Kamada, K. Ohta, I. Yoichiro, K. Kondo, Chem. Phys. Lett. 372 (2003).