Published in final edited form as:

Proc SPIE Int Soc Opt Eng. 2011 August 23; 8173: . doi:10.1117/12.899781.

Spectrally Resolved Femtosecond Photon Echo Spectroscopy of Astaxanthin

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Abstract

We have studied the coherence and population dynamics of Astaxanthin solution in methanol and acetonitrile by spectrally resolving their photon echo signals. Our experiments indicate that methanol has a much stronger interaction with the ultrafast dynamics of Astaxanthin in comparison to that of acetonitrile.

INTRODUCTION

Developments in nonlinear spectroscopy and its various applications in time and frequency domain techniques have been giving valuable information about the dynamics of the molecules at a variety of time scales. Use of multiple computer-interfaced delays for controlling coherence and population times provides population relaxation time, dephasing time, inhomogeneous broadening and vibrational structure of transient species. Coherent nonlinear spectroscopy using multiple femtosecond pulses is capable of providing detailed dynamical and spectroscopic information even in the presence of strong inhomogeneous broadening. Spectrally resolved one-color and two-color three pulse photon echo (SRPE) spectroscopy in the visible region were used for probing vibrational and electronic dynamics of simple and complex molecular systems [1-5]. Temporally resolving the photon echo spectra for different excitation wavelengths gives detailed information about the induced nonlinear polarization.

Astaxanthin is a carotenoid and belongs to a larger class of phytochemicals known as terpenes. It is classified as a xanthophyll. Astaxanthin can be found in microalgae, yeast, salmon, krill, shrimp, crustaceans and feathers of some birds. Astaxanthin is also a powerful antioxidant. Astaxanthin has eleven conjugated C=C bonds but two of them are located in cis orientation at the terminal rings that increase conformational disorder resulting in larger inhomogeneous broadening [6]. Additionally, this conjugation extends to the carbonyl groups, which usually alter the excited state properties and leads to further broadening of the linear absorption spectra [7-9]. Using the three-pulse photon-echo technique we not only probe the detailed dynamics of this system but also elucidate solvent effects.

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2. THEORITICAL BACKGROUND

Photon echo experiments are based on a non-collinear four wave mixing scheme with a specific phase matching function, where the incident beams propagate non-collinearly as shown in Figures 3 and 4, where three pulses are used. These three pulses are comprised of two pump pulses with wave-vectors k_1 , k_2 ; and a probe pulse with wave-vector k_3 . The first pulse coherently excites the molecule at optical transition and the second pulse k_2 interacts with the freely evolving system, giving rise to a population grating in the phase matching direction. The population grating spacing depends on the time interval between the first and second pulses, i.e. the coherence time t_{12} . A third pulse k_3 separated from second pulse by time t_{23} gets scattered due to the population grating and an echo signal is emitted in the direction, $k_s = -k_1 + k_2 + k_3$. The non-collinear phase matching method has the advantage that signal is spatially separated from the incoming fields.

In four-wave mixing spectroscopy, external field $E(t)$ is given by

$$E(t) = E_1(t + t_{12} + t_{23}) \cdot e^{ik_1 \cdot r - i\omega_1 t} + E_2(t + t_{23}) \cdot e^{ik_2 \cdot r - i\omega_2 t} + E_3(t) \cdot e^{ik_3 \cdot r - i\omega_3 t}$$

where, $E_j(t)$, ω_j and k_j denote time profile, mean frequency and wave vector of the j^{th} incident field. The third order nonlinear polarization is related to the third order response function $R^{(3)}$ through the relation [10].

$$P^{(3)} = \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 E_1^*(t + t_{12} + t_{23} - t_2 - t_1) \times E_2(t + t_{23} - t_3 - t_2) \times E_3(t - t_3) \times R^{(3)}(t_3, t_2, t_1)$$

And the measured nonlinear signal is given by

$$S(t) \sim |P^{(3)}(t)|^2$$

We consider here the signal from the direction $k_s = k_3 + k_2 - k_1$ and $\omega_s = \omega_1 = \omega_2 = \omega_3$. To obtain information about the temporal evolution of nonlinear polarization, the spectrum of the echo signal can be recorded. Then the frequency domain third order nonlinear polarization is obtained by Fourier transformation of $P^{(3)}$ with respect to t , i.e.

$$P^{(3)}(\omega, t_{12}, t_{23}) = \int_{-\infty}^{\infty} P^{(3)}(t, t_{12}, t_{23}) e^{i\omega t} dt$$

The time integrated frequency domain signal field radiated by the polarization $P^{(3)}$ is given by

$$E_s(\omega, t_{12}, t_{23}) \propto [2\pi i l n(\omega) c] P^{(3)}(\omega, t_{12}, t_{23})$$

where $n(\omega)$ is the real part of the refractive index of the sample at frequency ω and l is the length of the sample and c is the speed of light. The intensity of spectrally resolved photon echo signal is then given by [11].

$$S_{SRPE}(\lambda_d, t_{12}, t_{23}) \propto |E_s(\omega, t_{12}, t_{23})|^2 \propto |P^3(\lambda_d, t_{12}, t_{23})|^2$$

where λ_d is the detection wavelength that is used to amplify the echo signal emerging along the k_s direction.

3. EXPERIMENTAL SETUP

We use a commercial Ti:Sapphire multipass amplifier (ODIN, Quantronix Corp.) that is pumped by a Nd:YAG laser operating at 1 KHz (Corona, Coherent Inc.) and seeded by 20 fs pulses at a wavelength of 800 nm from a Ti:Sapphire oscillator (KM Labs.). The amplified laser generated 40 fs pulses at the central wavelength of 806 nm, which was used to pump a commercial computer-controlled travelling-wave optical parametric amplifier (TOPAS, Light Conversion Ltd.). In the optical parametric amplifier (OPA), a small fraction of the pump from multipass amplifier was used to generate the parametric super fluorescence seed in a thick BBO crystal. The OPA generated 50 fs pulses that were tuneable across the visible region of the spectrum. The output of the OPA is divided into three-beams of nearly equal intensity through ultrafast beam splitters and sent through variable delay lines consisting of retro-reflectors and motorized translations stages. The pulses were combined in boxcar geometry, i.e. with pulses placed on three corners of a square of 1cm length. The three pulses are finally attenuated and focused using an achromatic lens of 20 cm focal length on the sample of unit optical density, flowing in a fused silica flow-cell of 200 μ m path length. Teflon tubing was used in the flow-cell setup and a peristaltic pump was used to circulate the sample, such that a fresh portion of sample interacted with the pulses every time. It was important to flow the sample to avoid the decomposition of sample. The focussing is done in a square geometry into the flowing sample, wherefrom the echo-signal appear at the fourth corner of the square which is collected and is fiber-coupled into the Ocean-optics Spectrometer (HR-2000).

Astaxanthin was obtained from Sigma-Aldrich and the solutions were made in both methanol and acetonitrile with 10^{-4} molar concentration. The sample was flowed in a 0.2 mm path length flow cell that was circulated by a peristaltic pump.

4. RESULTS

The spectrally resolved plots by scanning the population time at fixed coherence times of 0, 50, 100 and 200 fs, for Astaxanthin in methanol is shown in Figure 5. At zero coherence time, the spectrally resolved contour plot shows a tilted profile which implies red-shifting of the photon echo signal during positive coherence time and blue shifting of the photon echo spectrum during negative population times. The inhomogeneous broadening was long enough such that even during longer coherence times, the contour plot did not become circular. But interestingly, there was clear shift in the center wavelength of the echo signal as the coherence time was varied from 0 to 200 fs. The photon echo spectra shifted its central wavelength from 510 nm at 0 fs to 520 nm at 200 fs. The peak shift was observed to be around 53 fs, 80 fs and 140 fs for both coherence and population time scans.

For Astaxanthin in acetonitrile, excitation pulses with center wavelength at 500 nm were used. The spectrally resolved photon echo signal at zero population time and at fixed zero coherence time was centered at 500 nm, while a blue shift was observed for negative coherence times and red shift for positive coherence times. These results are shown in Figure 6. The signal extended up to 200 fs during zero coherence time. At the coherence time of 50 fs, the contour plot shows only a slight red shift at positive population times. At the fixed coherence time of 100 fs, the spectrally resolved signal showed no wavelength shift indicating that spectral diffusion process occurred within 100 fs.

Furthermore, as can be seen from Figure 6, no peak shift was observed while the population time was scanned for Astaxanthin in acetonitrile. The S_1 and S_2 timescales for Astaxanthin in methanol are roughly 5 ps and 140 fs respectively, which matches with the previously published literature [12]. However, for Astaxanthin in acetonitrile, we find the S_1 and S_2 timescales are about 5 ps and 180 fs respectively. This is in contrast to the earlier analysis of the dynamics of the excited-state decay processes which indicated that the S_1 and S_2 lifetimes of Astaxanthin are independent of solvent [13].

5. CONCLUSION

The wavelength shift observed in the photon echo spectra observed for the spectrally resolved signal plots for astaxanthin in methanol and acetonitrile is due to the relaxation dynamics of the population. The tilt observed in the contour plots for early population and relation times is indicative of the inhomogeneous broadening. Our transient grating experiment, *i.e.*, for scans of coherence time at fixed zero population time indicated that no broadening of the spectra occurs during this time though the earlier reported experiment [12] indicated a broadened blue-shift observed in their spectrally resolved transient grating data, which they interpreted as a result of double quantum coherence pathways. This discrepancy can perhaps be understood in the light of the fact that the earlier reported experiments were conducted with a non-collinear parametric amplifier generating 40fs pulses. Such short pulses are amenable to greater chirp effects in the pulses which may result in the spectral broadening observed during the negative coherence times. Also, our data for various fixed coherences but at varying population times indicated no such larger broadening in any of the spectrally resolved photon echo contour plots indicating that energy gap fluctuations occurs in acetonitrile at a much faster time scale compared to the astaxanthin in methanol.

ACKNOWLEDGEMENTS

We thank the Wellcome Trust International Senior Research Fellowship (UK) funds and CSIR India for financial support.

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Figure 2.

Energy level scheme for the Astaxanthin molecule. A is the linear absorption, while k_1 and k_2 are decay constants associated with the decay of states S_1 and S_2 .

Figure 3.
Schematic diagram of photon echo experiment.

Figure 4.
Pulse sequence for three pulse photon echo experiment.

Figure 5.
Excitation at spectrally resolved photon echo plots for astaxanthin in methanol taken while scanning the population time for various coherence times t_{12} .

Figure 6.

Excitation at spectrally resolve photon echo plots for astaxanthin in acetonitrile taken while scanning the population time for various coherence times t_{12} .