

Transient-grating Stark Spectroscopy

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Abstract: We describe a novel nonlinear spectroscopy that combines the high signal-to-noise of heterodyne-detected transient-grating spectroscopy with Stark spectroscopy, enabling sensitive detection of charge transfer kinetics. We demonstrate the method on the carotenoid fucoxanthin.

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1. Introduction

Characterizing ultrafast energy and charge transfer is important for our understanding systems ranging from natural photosynthetic complexes to organic semiconductors. Distinguishing the kinetic processes of energy transfer and charge separation in such systems is challenging due to the lack of clear spectral signatures of charge transfer states, which are typically nonradiative. In Stark spectroscopy the application of a large external field can be used to affect any processes that involve the movement of charge [1]. Linear Stark spectroscopy has proven to be a valuable method for uncovering charge transfer (CT) states in photosynthetic reaction centers [2, 3] and other systems [1, 4]. Pump-probe spectroscopy in the presence of strong external electric fields has been used to study the kinetics of charge transfer and recombination in biological [5] and organic semiconductor systems [6, 7]. The magnitude of the electric-field-dependent kinetics is often small [5], necessitating a sensitive spectroscopic method. Heterodyne-detected transient-grating spectroscopy offers significant signal-to-noise improvements over pump-probe spectroscopy [8]. We propose a new transient-grating Stark (TG Stark) spectroscopy to enable sensitive, high time-resolution detection of charge transfer kinetics. We demonstrate the method on the carotenoid fucoxanthin in solution at 77 K.

2. Methods

The experimental setup and pulse sequence for TG Stark spectroscopy is shown in Figure 1A. The output of a regenerative amplifier is used to pump two, dual-stage non-collinear optical parametric amplifiers (NOPAs) [9] to provide the pump (centered at 470 nm, 40nm bandwidth) and probe (centered at 530 nm, 60 nm bandwidth) pulses; each is then compressed with a grism compressor. The pump is chopped, and the probe is delayed relative to the pump by delay τ using a retroreflector on a linear stage. Pump and probe are focused on a diffractive optic, to generate the background-free passively-phase-stable TG geometry and a delayed local oscillator for heterodyne detection [8]. The beams are spatially overlapped and focused in a Stark sample cell in a liquid nitrogen immersion cryostat (Janis) [10]. The sample, fucoxanthin (Sigma Aldrich) was dissolved in a 50/50 mixture of ethanol/glycerol and loaded into the custom sample cell composed of conductive (ITO) coverslides separated by a 100 μm Teflon spacer to give an optical density of 0.3. A 250 Hz square-wave (50% duty cycle) signal synchronized to the laser trigger is used to drive a high voltage power supply that induces an external electric field of ~ 0.5 MV/cm in the

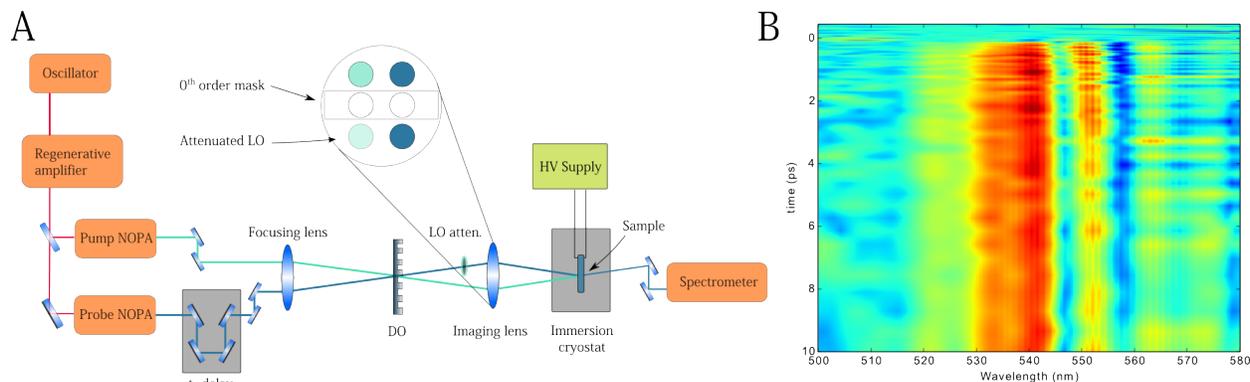


Figure 1. A: Experimental setup for Stark transient-grating spectroscopy. B: Absolute value transient-grating Stark spectrum of fucoxanthin in 50/50 ethanol/glycerol at 77K (differential measurement comparing TG signal with and without Stark field).

sample. The heterodyned signal is detected with a spectrometer (Horiba Jobin Yvon iHR320 and Pixis 100B CCD) at 500 Hz. The pump chopped at 500 Hz and E-field chopped at 250 Hz produces a four-phase signal that is used to obtain the Stark-shifted transient grating signal, resolved in time by scanning τ .

3. Results

Figure 1B shows preliminary Stark TG data in fucoxanthin, resolved as a function of probe wavelength and delay time τ . The acquisition time for each Stark TG spectrum (at a given τ delay) was 5 seconds, demonstrating that the Stark TG signal is readily detectable. We expect the method to provide a high sensitivity spectroscopic probe of charge transfer processes in a wide range of systems.

4. References

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