

Two-dimensional electronic femtosecond stimulated Raman spectroscopy

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Abstract. We report two-dimensional electronic spectroscopy with a femtosecond stimulated Raman scattering probe. The method reveals correlations between excitation energy and excited state vibrational structure following photoexcitation. We demonstrate the method in rhodamine 6G.

Two-dimensional electronic spectroscopy (2DES) has emerged as an attractive method for studying the ultrafast dynamics and electronic structure of a wide range of condensed matter systems [1]. Femtosecond stimulated Raman spectroscopy (FSRS) [2-5] has provided an incisive structural probe of the primary motions in vision [6], proton transfer in GFP [7] and other charge transfer processes [8]. Here we combine these two methods, demonstrating 2DES with a FSRS probe (2DE-FSRS).

We have previously demonstrated pulse-shaping-based 2DES in the pump probe geometry [9], enabling the straightforward use of a continuum probe to expand the frequency information available in 2DES [10]. This versatile setup also allows the straightforward use of more sophisticated probes such as FSRS. In a standard FSRS experiment, a single actinic pump pulse is used. Thus there is no information available about the excitation frequency dependence of the observed FSRS signal. In 2DE-FSRS the actinic pump is comprised of a pair of pulses, separated by delay t_1 . A time t_2 following the actinic pulse sequence, a combination of narrowband Raman pump and continuum probe initiate stimulated Raman scattering. A differential measurement is made (actinic pump on and off) to obtain the FSRS modes excited as a result of the actinic pump. As in 2DES, Fourier transforming with respect to the t_1 delay resolves the excitation frequency, allowing correlations to be made between excitation and detection frequencies. Recording different 2DE-FSRS spectra as a function of waiting time t_2 will show how these correlations evolve.

The pulse sequence and experimental setup for 2DE-FSRS are shown in Figure 1A. Part of the output of a regenerative amplifier (Spitfire Pro, 800 nm, 1mJ pulses at 1 kHz) is used to pump a non-collinear optical parametric amplifier (NOPA) [11] to provide the actinic pump. The NOPA pulse is sent into an acousto-optic pulse-shaper (Dazzler, Fastlite), giving near transform limited pulses of 25 fs, centered at 530 nm. In addition to providing pulse compression, the Dazzler was used to create a pair of actinic pump pulses with variable delay t_1 . A continuum probe pulse is created by focusing a small fraction of the 800 nm pulse into a 2 mm thick sapphire window with a 200 mm focal length lens and collimated using a 250 mm spherical mirror. The Raman pump is obtained by spectrally filtering a portion of the 800 nm light with a combination of notch filters to produce ~ 1 nm pulses. The relative polarization of all pump and probe beams are parallel. A linear stage was used to generate the t_2 delay between the actinic pump pulses and the FSRS probe pulses. The pump beam was focused with a 250 mm fused silica lens to a spot size of 200 μm in a 300 μm thick sample cell.

The probe beam was focused with a 250 mm spherical mirror to a spot size of 100 μm and overlapped in the sample with the pump beam at a crossing angle of $\sim 2^\circ$. These focusing and excitation conditions produced a $\sim 70\%$ excitation level of the sample. Cross-correlation between the pump and probe pulses indicated a time resolution of ~ 200 fs. The pump beam was electronically “chopped” at 500 Hz by the Dazzler, and the probe beam was spectrally resolved at 1 kHz using a Horiba Jobin Yvon iHR320 spectrometer and Pixis 100B CCD camera. We note that in the experimental configuration shown here, both 2DES and 2DE-FSRS spectra are obtained simultaneously, as the Raman pump pulse is chopped.

2DE-FSRS data taken on rhodamine 6G in ethanol is shown in Figure 1B, for a waiting time $t_2 = 300$ fs. Along the detection frequency axis, several excited state Raman modes are clearly observed. In this system, we did not observe time dependent shifts of the observed modes, or excitation wavelength dependent features in the FSRS spectrum over the excitation wavelength range that was studied.

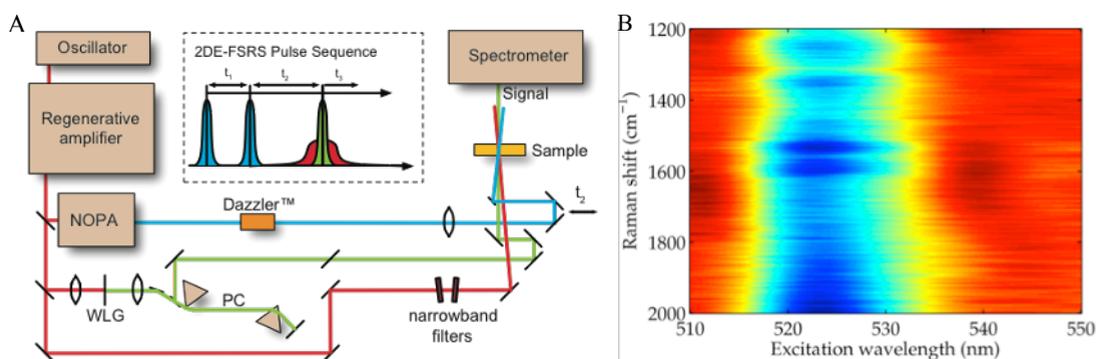


Fig 1: A: Experimental setup for 2DE-FSRS. (NOPA: noncollinear optical parametric amplifier, WLG: white light generation in a sapphire plate, PC: prism compressor) B: 2DE-FSRS spectrum of rhodamine 6G in ethanol at a waiting time of 300 fs.

By resolving the excitation frequency dependence of FSRS without compromising time resolution, 2DE-FSRS promises to provide a structural probe of excited states as they evolve. We note that the FSRS probe, being non-resonant, can access optically dark states such as charge transfer states that are invisible to 2DES and other resonant spectroscopies. In addition the broadband FSRS probe offers an attractive alternative to the relatively narrowband spectral data obtained in experiments using IR pulses. The combination of 2DES and 2DE-FSRS will provide complementary electronic and vibrational signatures of spectroscopic intermediates, facilitating their identification.

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