Solvation Stokes-Shift Dynamics Studied by Chirped Femtosecond Laser Pulses

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Laser setup

The femtosecond laser system used for this study consists of a regeneratively amplified Ti: Sapphire laser (Spitfire, Spectra-Physics) seeded by a 86 MHz Ti:Sapphire oscillator (KM Labs) having a spectral bandwidth of 40 nm (FWHM). The output from the amplifier at 1 kHz centered at 800 nm is ~ 700 μJ and was attenuated before entering a phase-amplitude pulse shaper (MIIPS Box 640, Biophotonic Solutions). The dispersed spectrum covered 600 SLM pixels with a resolution of 0.32 nm per pixel. The schematic of the setup is shown in Fig. S1. The output of the pulse shaper was frequency doubled by a 100 μm thick β-barium borate (BBO) crystal at the sample plane and the resulting second harmonic was spectrally filtered using an infrared cutoff filter (BG39).

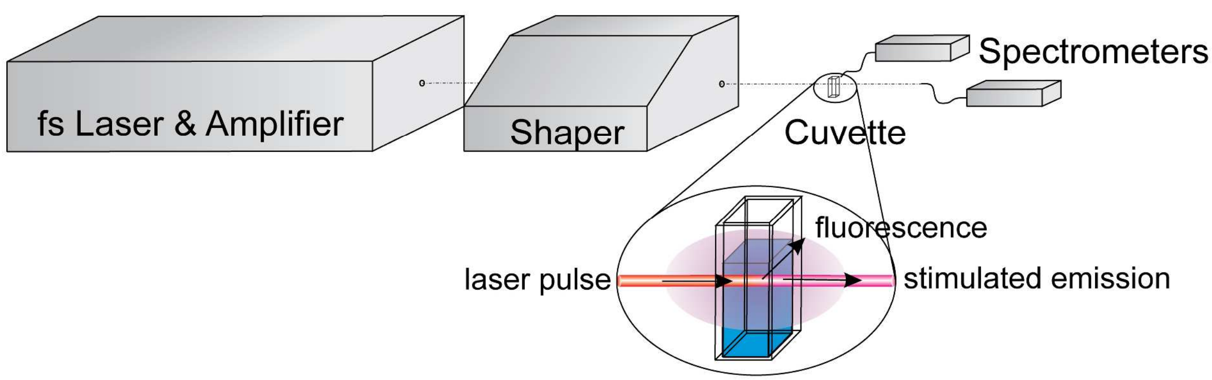


Figure S1. Experimental setup. The amplified output beam is attenuated and sent to a SLM based folded 4-f shaper.

High-order phase distortions introduced by the optics in the laser system as well as by the setup are compensated by the multiphoton intrapulse interference phase scan (MIIPS) software resulting in 36 fs (FWHM) transform limited (TL) pulses at the sample. Briefly, the MIIPS software introduces a series of calibrated reference phases and collects the resulting second harmonic spectrum for each. The collection of second harmonic spectra is then used to determine the second derivative of the phase distortions in the pulse. The software then introduces a phase designed to counteract the phase distortions in order to obtain TL pulses. The software tests the resulting pulses iteratively until phase distortions across the spectrum are smaller than 0.03 rad, a value reached in 3-6 iterations.

Value of Chirp Effect vs Probability of Excitation

We have used extremely low powers to perform the fluorescence detected chirp scans for IR 144 to establish the nature of effect at extremely low levels of excitation probabilities. Value of the effect [Max (Intensity of fluorescence) – Min (intensity of fluorescence)] / (Intensity of fluorescence of TL pulse) is plotted as a function of the probability of excitation. The probability of excitation is related to the laser fluence and is calculated as $P = F\sigma$ where $F = It/h\nu$ is the number of photons/cm^2 and σ is the absorption cross section at 800 nm, calculated to be $2.6\times10^{-16} cm^2$. In general if *Effect* = x^2 and *Intensity* = x, then *Effect/Intensity* = x. Thus the relative effect will be a linear function of excitation if the absolute effect is quadratic with respect to excitation. This is shown in Fig. S2

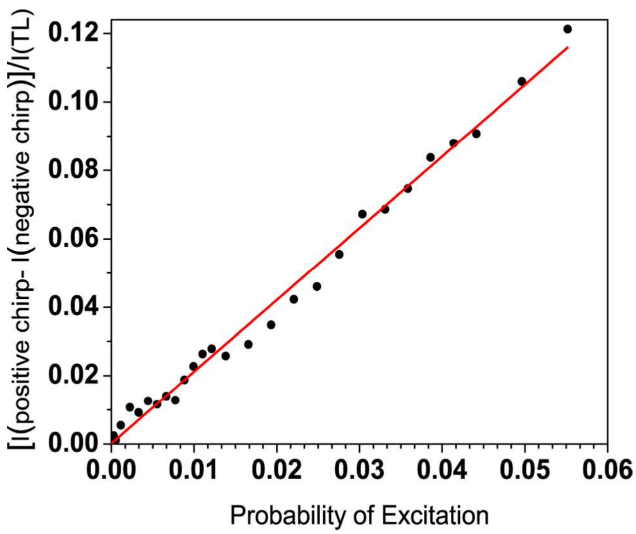


Figure S2. [Max (Intensity of fluorescence) – Min (intensity of fluorescence)] / (Intensity of fluorescence of TL pulse) plotted as a function of the probability of excitation for IR 144. Red line is the linear fit to the data.

The linear fit to the data intersects zero, supporting the fact that the effect disappears asymptotically i.e. it goes to zero, in contrast to previous claims of pure phase control of dye molecules under very low excitation powers. The lowest probability of excitation achieved in the experiment was 0.0002 i.e. 0.02% corresponding to the laser fluence of $2\times10^{-7} J/cm^2$ and the power flux of $5\times10^{-6} W/cm^2$. We see a pure second order effect of phase modulation corresponding to two photon non-linear optical processes.

Concentration Dependence of Stimulated emission

The concentration dependence of the stimulated emission of IR 144 was measured for concentrations ranging from 10^{-6} to 10^{-8} M. The stimulated emission was monitored along the direction of propagation of the laser. Fig. S3a shows the data points along with a quadratic fit to the data. The quadratic nature of the effect was further confirmed by plotting in a double log scale (Fig. S3b).

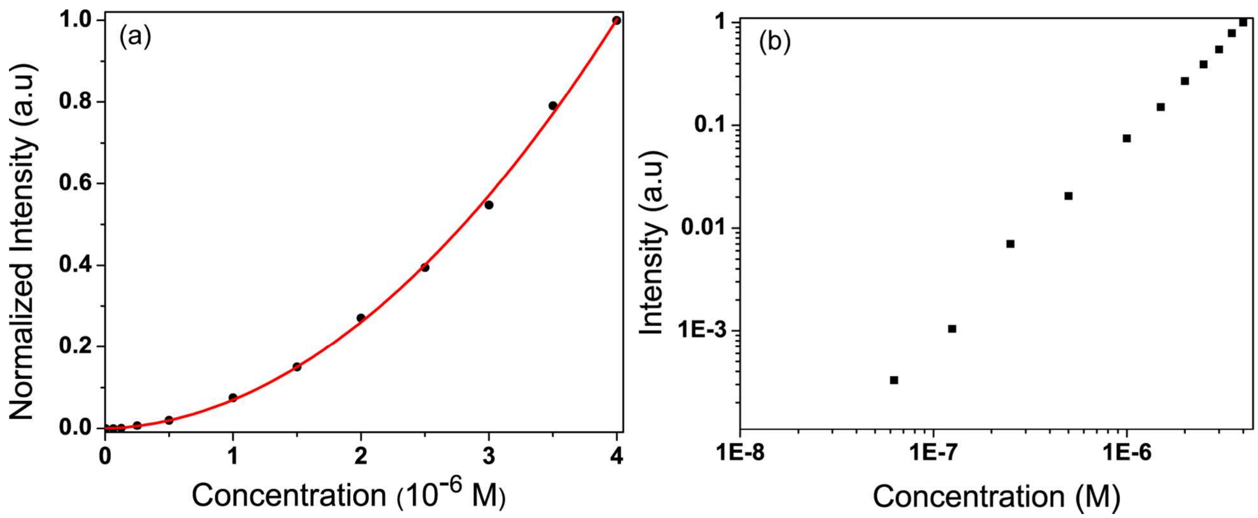


Figure S3. (a) Concentration dependence of the stimulated emission, Red curve is the fit to the data. (b) Double log plot for the same data, showing that one order of magnitude change in concentration causes two orders of magnitude change in the stimulated emission.

Spectra

The spectra of the femtosecond laser, fluorescence (detected at right angle) and stimulated emission (detected along the direction of propagation) of solution of IR 144 in methanol at room temperature are shown in Fig. S4. The emission spectra were recorded using a compact spectrometer (USB 4000, Ocean Optics).

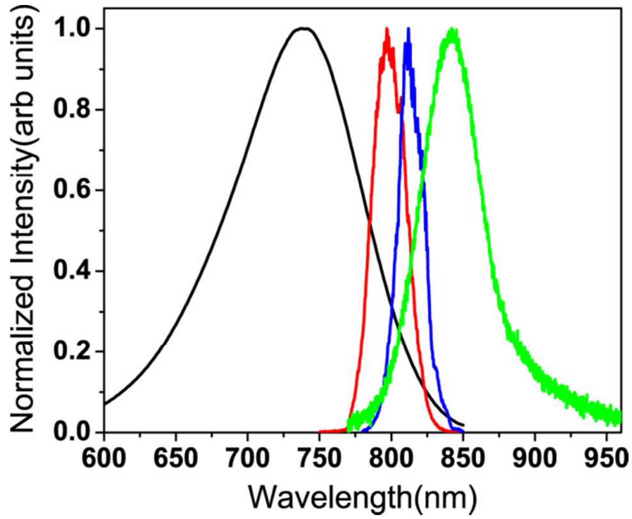


Figure S4. Absorption (black), spectra of the laser (red), fluorescence spectra (green), and coherence emission (blue).

Model of inhomogeneous broadening

The homogeneously filled inhomogeneous absorption and fluorescence spectra profiles used in the model together with the laser spectrum are shown in Fig. S5. To have the best agreement between the model and experiment the positions of the homogeneous lines in the inhomogeneous profiles must be symmetrical with respect to the center between them as marked on the figure. We put only 10 homogeneous lines for each state as an example to show clear separation between them. The simulated results will be the same with densely filled lines.

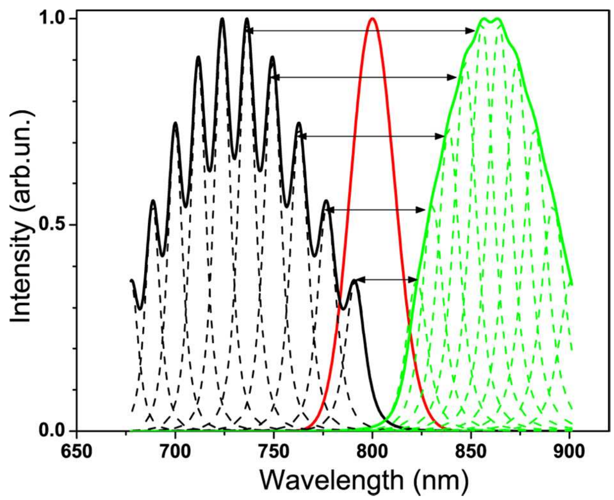
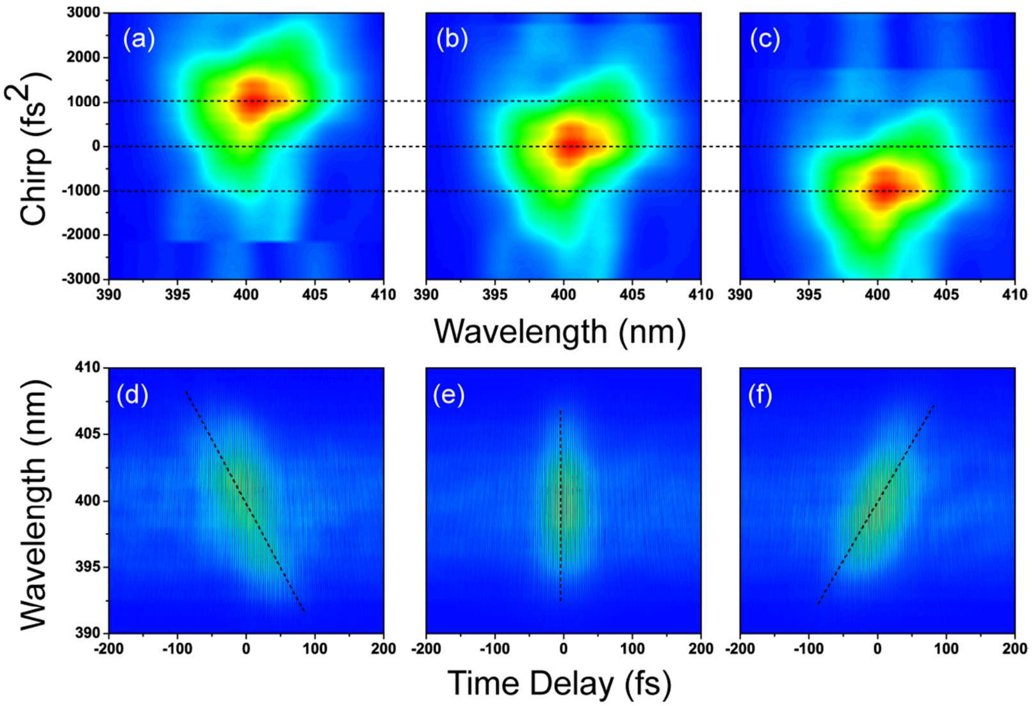


Figure S5. Spectra of the states in the upper directly excited state (black) and second relaxed exited state (green) used in the model together with laser spectrum (red). The symmetry of positions of corresponding states are marked with arrows.

Pulse shaping accuracy

We performed interferometric XFROG type of measurements on chirped and TL pulses to test the accuracy of the shaper in generating and measuring phase modulated pulses. MIIPS chirp scans were also performed to show that the corresponding chirp values are recovered.

Experimental



Simulation

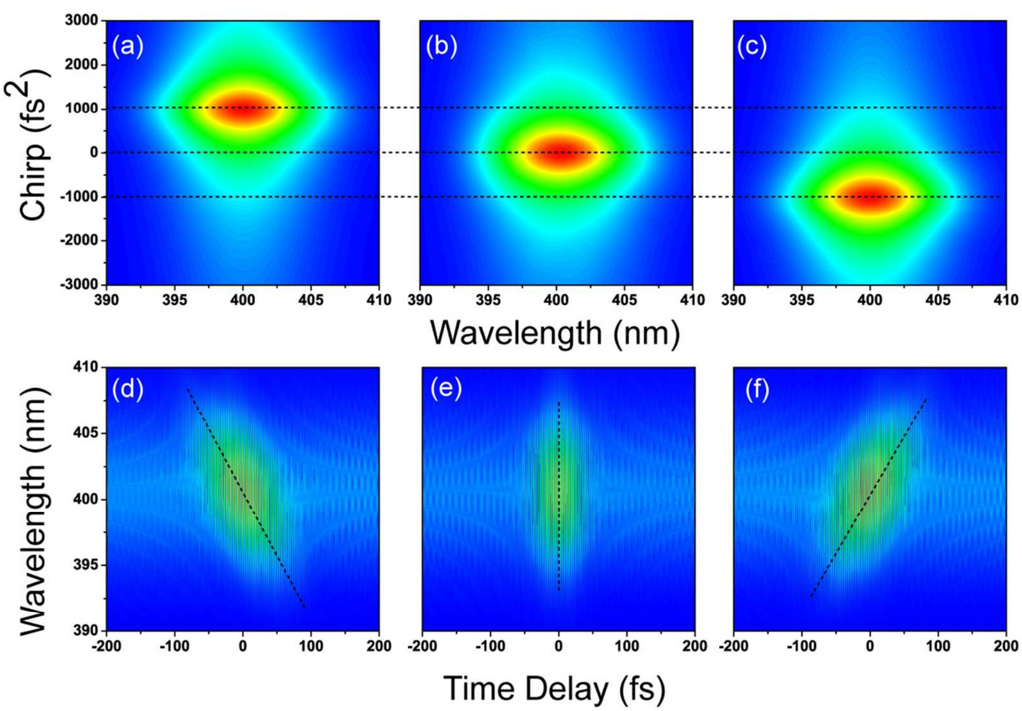


Figure S6. Experimental and Simulated plots showing the MIIPS chirp scans for (a) -1000 fs^2 chirped pulse (b) TL pulse (c) 1000 fs^2 chirped pulse. i-XFROG traces for (d) 1000 fs^2 chirped pulse (e) TL pulse and (f) -1000 fs^2 chirped pulse.