Supporting Information
for
Electronic dephasing of molecules in solution measured by nonlinear spectral inteferometry

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Importance of using transform-limited pulses free of high-order dispersion

Interferometric measurements require transform-limited pulses that are free of high-order dispersion. Any type of dispersion will cause interferometric features to be measured on time scales longer than the pulse duration. While second-order dispersion (linear chirp) is relatively easy to eliminate, third-order dispersion (TOD) is not easy to measure and compensate. Figure S1 shows the SHG interferometric autocorrelation trace for pulses having 10^5 fs^3 TOD. Notice that long-lived out-of-phase interference is observed, however, this is all part of the pulse structure. Here we highlight that TOD produces characteristic π-phase steps that are part of the pulse structure and are not to be correlated with the system being measured.

The SHG autocorrelation of TL pulses, free from high order dispersion, is shown in Figure S1b. The random jumps in the extracted phase are due to low signal-to-noise level past 90 fs. The retrieved temporal intensity confirms the absence of any amplitude beyond 90 fs, which is not the case for pulses with TOD, which show amplitude beyond 90 fs.

Forward emission power and concentration dependence

The power dependence curve for stimulated emission shows a quadratic dependence with some amount of cubic as shown in Figure S3a. The signal also depends linearly with the sample concentration. Both these dependence support the assignment of the signal as the heterodyned detection of a $\chi^{(3)}$ process.

Fitting of fundamental and fluorescence signals

The experimental interferograms for laser fundamental and forward emission is fit using the phenomenological formulas described in the main text.

Phase extraction from interferogram

The forward emission interferogram were Fourier transformed to extract the phase and amplitude information. Figure S2 shows the gradual π shift in phase (red dots) overlaid on the oscillatory signal for IR144.

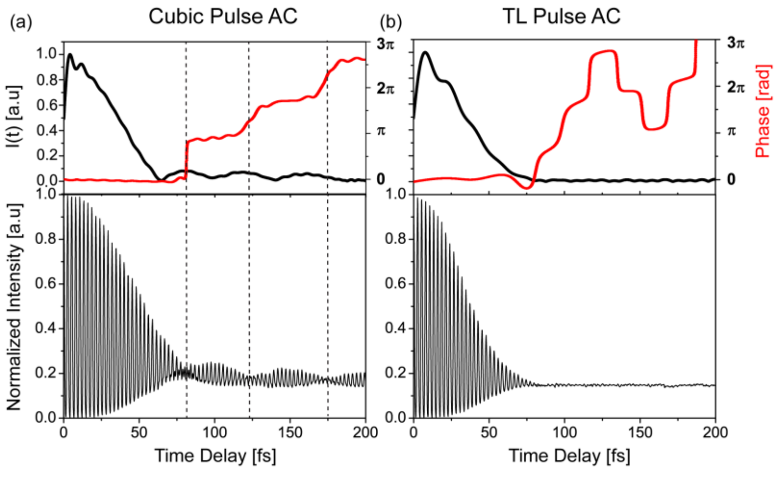

Figure S1. Experimental SHG Interferometric AC plot (bottom) and the corresponding phase change (red) and retrieved amplitude (black) during the measurement for pulses having (a) 10^5 fs^3 cubic phase and (b) transform limited pulses. The dashed lines serve a guide to the pi phase change positions.

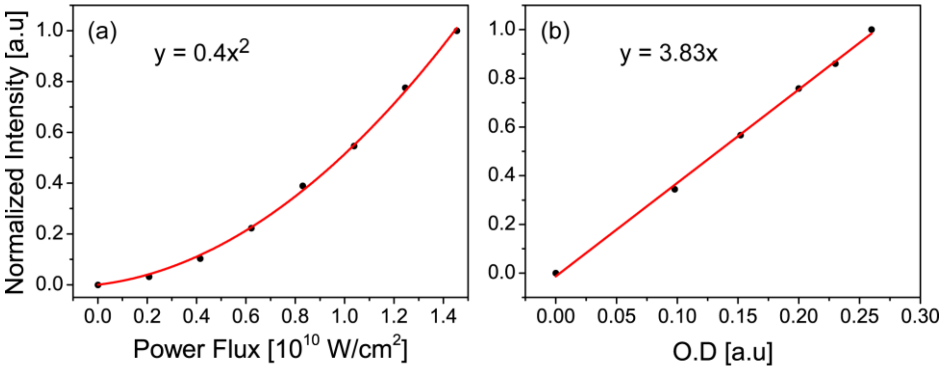

Figure S2. Experimental (a) power dependence and (b) concentration dependence curve for stimulated emission.

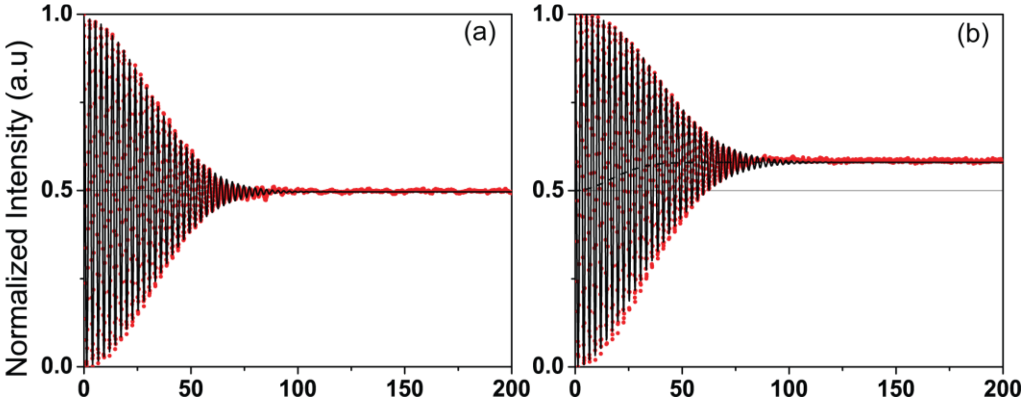

Figure S3. Experimental data points (red) and the corresponding fit (black) for the (a) laser fundamental and (b) fluorescence for IR144.

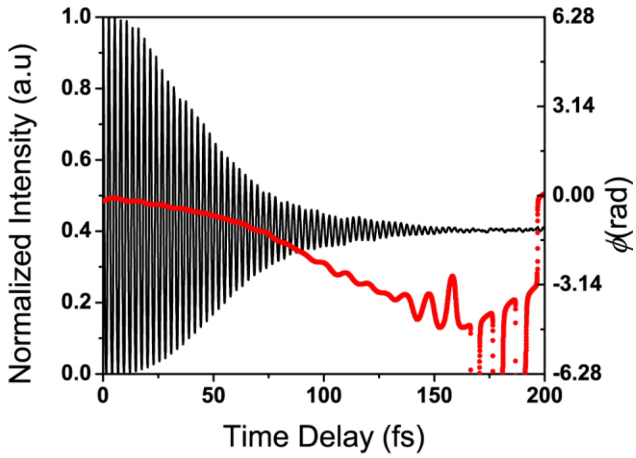

Figure S4. Extracted phase (red) and forward emission interferogram (black) for IR144.

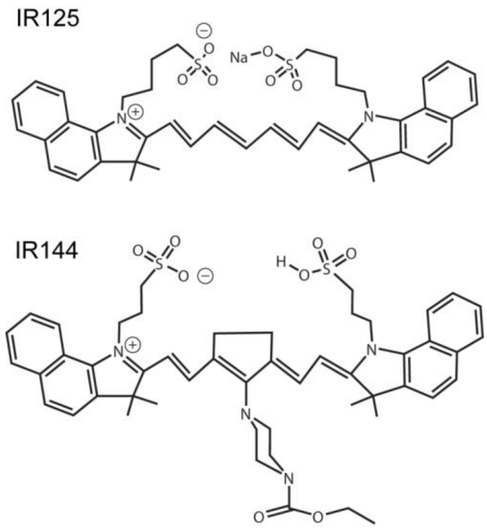

Figure S5. Structures of IR125 and IR144.