

# Supporting Information

## **Ultrafast relaxation dynamics of photoexcited Zn-porphyrin: electronic-vibrational coupling**

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## **Sample Preparation**

Fresh solutions are prepared daily of Zinc-tetraphenylporphyrin (Zn-TPP, Strem Chemicals) dissolved in spectrophotometry-grade tetrahydrofuran (THF) (Fisher Scientific, Optima<sup>tm</sup>). THF was chosen due to its mid-range polarity,<sup>1</sup> clean Raman spectrum,<sup>2</sup> and the high solubility of the analyte. Time-resolved measurements are carried out in a 1 mm path length cuvette with stopper (Starna) at concentrations of 50  $\mu\text{M}$  for transient absorption and 100  $\mu\text{M}$  for pump-DFWM.

## **Apparatus**

Steady-state excitation and emission spectra are recorded with a spectrofluorometer (Horiba, Fluoromax-4). Steady-state absorption spectra are acquired through a UV-Vis fiber spectrometer. Mass spectrometry is performed using liquid injection field desorption ionization (LIFDI).

Transient absorption measurements are achieved using a home-built noncollinear optical parametric amplifier (NOPA) as a tunable pump and using supercontinuum produced from a sapphire plate as a white-light probe. Cross-correlation of pump and probe pulses

is representative of the instrument response function (IRF), and is kept at 25 fs by prism compressors in each beam path. Pump and probe beams are set to magic angle polarization difference ( $54.7^\circ$ ) to avoid measurement of orientation-dependent dynamics. A lock-in amplifier and monochromator (Oriel, CS260) are used for detection.

Pump-degenerate four-wave-mixing (pump-DFWM) measurements are carried out using two NOPAs. The output of one NOPA is split into three pulses forming a DFWM probe sequence in a BOXCARS phase matching geometry, generating a spatially separated signal.<sup>3</sup> Delay between the pump and Stokes pulses within the sequence is set to zero, while the probe delay is varied by a piezo stage ( $t$ ). DFWM pump and Stokes pulse energies are kept to 50 nJ and probe to 30 nJ. A second NOPA produces the preceding pump pulse resonant with  $S_0 \rightarrow S_2$  absorption, which travels through an independent delay stage ( $T$ ). The time ordering and beam geometry are depicted in Figure S1. The DFWM pulses are tuned into resonance with the sample's excited-state absorption at 510 nm (Figure S2), and have a temporal FWHM determined by autocorrelation to be 12 fs. There is no spectral overlap between pump and probing sequence pulses. The energy of the initial pump pulse is 200 nJ in both pump-DFWM and transient absorption. Pump and probe spot sizes are 300  $\mu\text{m}$  and 80  $\mu\text{m}$  respectively at their focal points. A photomultiplier tube (Hamamatsu) and monochromator are used for signal detection, and a chopper wheel blocks every other pump pulse to allow for shot-to-shot subtraction of nonresonant contributions to the signal.

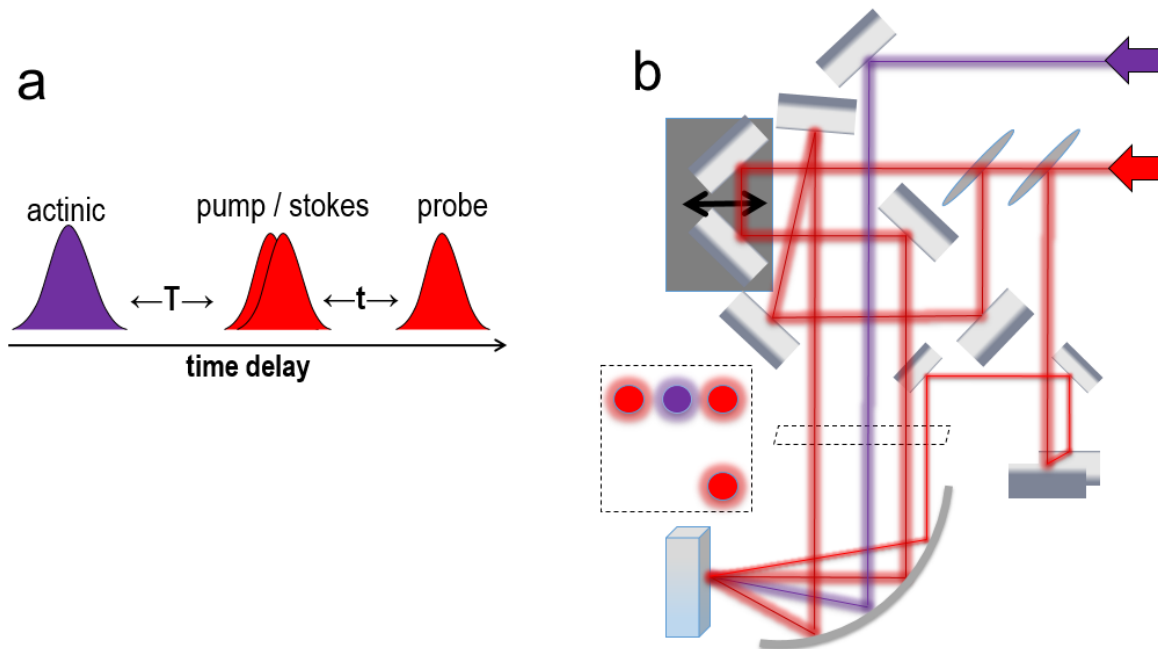


Figure S1: The time ordering of the pump-DFWM sequence (a) consists of an initial actinic pulse to promote the system to an electronically excited state followed by a set of pulses that generate a DFWM signal on the excited state. Evolution of the excited state is followed by varying  $T$  and wavepacket dynamics are followed by scanning  $t$ . In the depicted optical setup (b), one beam passes through two beamsplitters and a variable delay stage to produce the three DFWM pulses incident on the sample in a phase-matched BOXCARS geometry, and the path of the actinic pulse is directed onto the shared parabolic focusing mirror.

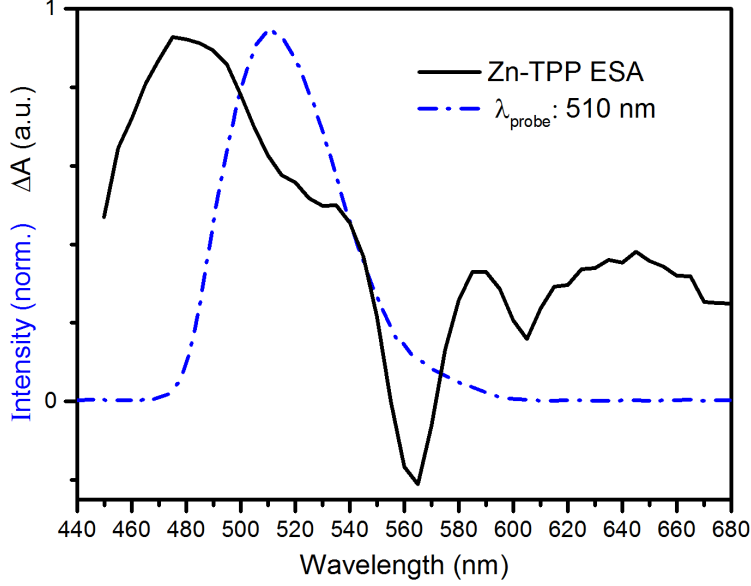


Figure S2: The DFWM pulse sequence is centered at 510 nm in order to achieve resonance with the excited-state absorption (ESA) of Zn-TPP. The ESA spectrum was obtained using a 420 nm pump and 500 fs delay. Probing with DFWM in this region also avoids spectral overlap with the actinic pulse and  $S_0 \rightarrow S_2$  ground-state Soret absorption.

## Signal Analysis

Transient absorption signals measured at an individual wavelength ( $\sigma_\lambda$ ) are fit with the expression

$$\sigma_\lambda = \sum_{i=0}^n A_i^\lambda N_i \quad (1)$$

where the independent amplitude at each wavelength and the population of each state are represented by  $A_i^\lambda$  and  $N_i$  respectively. The number of states involved in the dynamics are represented by the  $n$  terms of the summation in equation (1). This parameter is held to the minimum value that allows for fitting the signals at all wavelengths without a systematic deviation of the residuals. The total signal at a given wavelength therefore composed of weighted contributions from the population of each state. Each state's time-dependent population is obtained by solving a set of linear rate equations allowing for parallel and sequential decays which represent the relaxation model, i.e.

$$\frac{dN_0}{dt} = -Bg(t) + \sum_j \frac{1}{\tau_n} N_n \quad (2)$$

$$\frac{dN_1}{dt} = Bg(t) - \sum_k \frac{1}{\tau_1} N_1 \quad (3)$$

$$\frac{dN_i}{dt} = \sum_l \frac{1}{\tau_{i-1}} N_{i-1} - \sum_m \frac{1}{\tau_i} N_i \quad (4)$$

where  $\tau_i$  denotes the time constant associated with a state's  $N_i \rightarrow N_{i+1}$  population transitions. The term  $Bg(t)$  in (2) and (3) acts as a source representing the pump pulse, and is composed of amplitude  $B$  and the Gaussian envelope:

$$g(t) = \exp \left[ -4 \ln(2) \left( \frac{t - t_0}{W_{IRF}} \right)^2 \right] \quad (5)$$

The pulse function considers  $W_{IRF}$  as the full width at half maximum of the IRF. The fitting procedure seeks to find a set of parameters  $\{A_i^\lambda, \tau_i\}$  that produce the best global fit.

Pump-DFWM signals are recorded as oscillations in the time domain at a selected detection wavelength and pump delay. Consecutive measurements with the pump beam incident on the sample and blocked from the sample are subtracted from each other to isolate the resonantly enhanced signal. The initial 40 fs of oscillation are discarded to remove the coherent artifact. The signal is zero-padded before a fast Fourier transformation is performed and a frequency spectrum is produced.

## Steady State Measurements

Steady state absorbance spectra of Zn-TPP dissolved in THF were measured to check for aggregation. Solutions of 1  $\mu\text{M}$  concentration are thought to be below the aggregation threshold.<sup>4</sup> The Soret absorption profile was measured for a series of solutions of concentrations ranging from 1  $\mu\text{M}$  to 100  $\mu\text{M}$ , and no broadening or shifting was observed, as shown in Figure S3. No evidence of J-aggregation was found in this concentration range of THF based solutions.

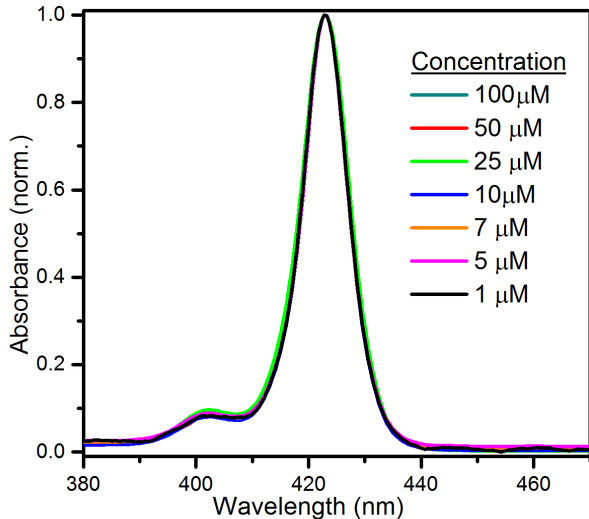


Figure S3: The Soret absorption profile is unaltered over the range of concentrations measured. There is no evidence of J-aggregation at concentrations up to 100  $\mu\text{M}$ .

Fluorescence excitation-emission matrices were collected for further assurance of sample solution purity. The concentration range is extended one order of magnitude below that of

the steady state absorption measurements. No change in fluorescence profiles was observed in the range of 0.1  $\mu\text{M}$  to 5  $\mu\text{M}$ , displayed in Figure S4. Since 0.1  $\mu\text{M}$  solutions are well below the expected concentration threshold for aggregation, the unchanging fluorescence spectra can be taken together with the absorbance measurements and their overlapping concentration ranges to ensure that there is no appreciable aggregation of solutions up to 100  $\mu\text{M}$ .

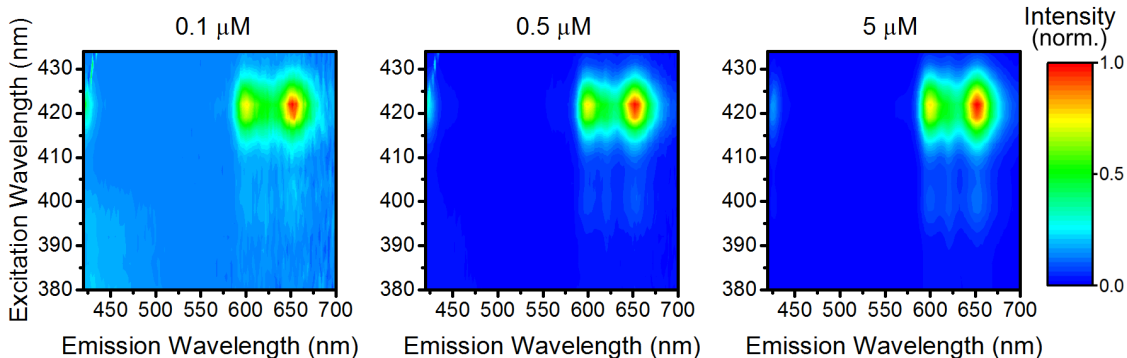


Figure S4: Fluorescence excitation-emission matrices of Zn-TPP solutions in THF do not exhibit broadening of the Soret or Q bands over a 50 fold concentration change.

LIFDI mass spectrometry was carried out on the sample after optical measurements were performed to check for sample purity and degradation and results are displayed in Figure S5. This soft ionization technique causes minimal fragmentation and signal is readily obtained from molecular ions.<sup>5</sup> No peaks were present in the calculated  $m/z$  region for demetallated Zn-TPP, suggesting that the molecules in solution did not suffer from loss of the central zinc atom to any significant degree. One isotopic pattern was predominantly detected, which is attributed to the Zn-TPP molecular ion, and no patterns from expected photoproducts were found. These qualitative results provide evidence that the sample did not undergo any appreciable chemical degradation.

## Transient Absorption Measurements

The relaxation processes and states involved in the dynamics of photoexcited Zn-TPP are illustrated in Figure S6, along with their contributions to the transient absorption signals recorded at representative wavelengths after 420 nm excitation. In agreement with prior measurement,<sup>6</sup> global fitting produces five time constants and six involved states, modeled as follows: relaxation of  $S_2$  ( $\tau_1 = 70$  fs),  $S_2 \rightarrow S_1$  internal conversion (IC) ( $\tau_2 = 1.8$  ps), vibrational relaxation (VR) in  $S_1$  ( $\tau_3 = 10$  ps,  $\tau_4 = 100$  ps), and  $S_1 \rightarrow T_1$  intersystem crossing (ISC) ( $\tau_5 = 1.8$  ns). Ground state bleach (GSB) appears within the IRF as a negative contribution at 550 nm and is assigned in agreement with the steady state absorption spectrum. Excited state absorption (ESA) from  $S_2$  and  $S_1$  appears as a positive contribution at every wavelength. The time constant for ISC corresponding to the contribution at each wavelength from the triplet state is set by the measured Zn-TPP fluorescence lifetime in THF.

The transient absorption map recorded after 430 nm excitation is shown in Figure S7. In contrast to the map measured using a 420 nm pump, no blue-shift of the negative signal

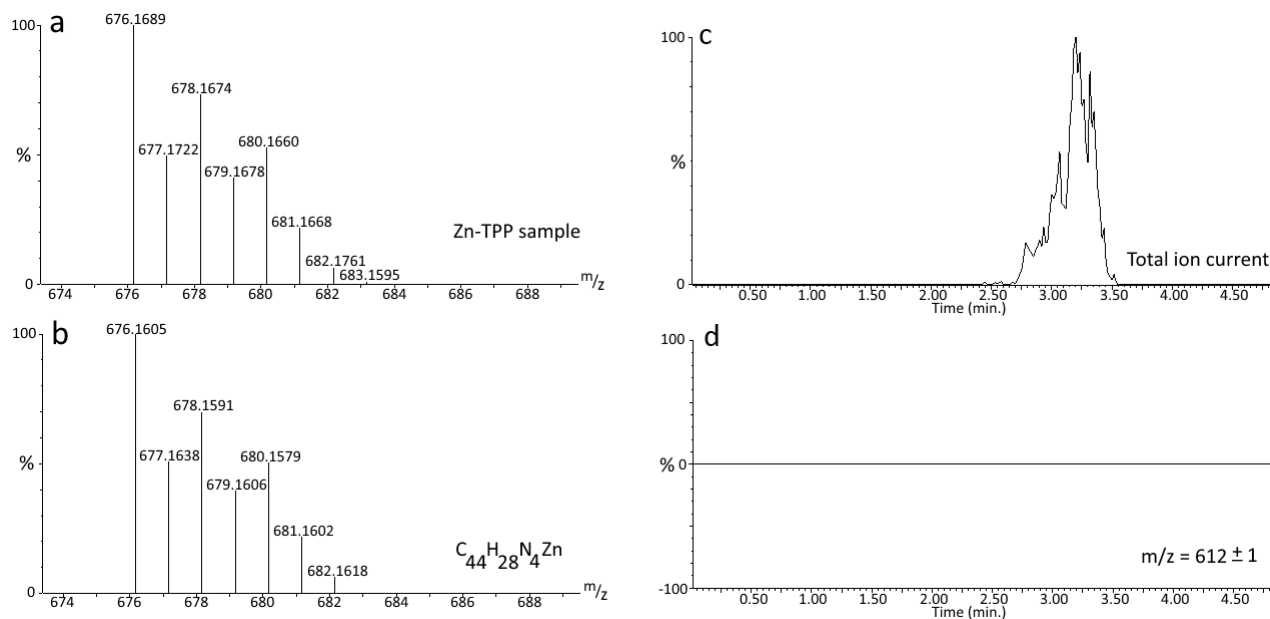


Figure S5: The LIFDI-MS spectrum of the sample shows the isotopic pattern obtained over the course of the measurement (a) is identical to the calculated pattern for the Zn-TPP (b). Monitoring the field desorption spectrum (c) for demetallated Zn-TPP as current is increased produces no ion peaks (d).

is observed around 560 nm. Fitting kinetic traces at representative wavelengths in the same manner as explained above reveals a loss of the fast time constant, consistent with excitation to a cold  $S_2$  state. When subtracted from the transient absorption map recorded after excitation at 420 nm a nonzero difference is obtained that highlights the time-dependent redistribution of energy from the higher energy pump.

Figure S8 illustrates that the spectrally shifting zero point in the difference transient absorption map between using 420 nm and 430 nm pump pulses may be attributed to relaxation of a vibrationally hot excited state, as described in the main text. The simulated transient absorption maps of a vibrationally hot state, which blue-shifts as the ESA energy gap widens during relaxation, and a non-shifting signal representing the fully relaxed state are subtracted from one another. The result is a crossing point in the difference map that shifts in energy.

## Pump-DFWM Measurements

As the  $1350\text{ cm}^{-1}$  vibrational mode of the excited state shifts in frequency immediately following 420 nm photoexcitation, there is an accompanying rise in intensity. The intensity of the peak maximum during the initial dynamics is shown in Figure S9 for the two prominent molecular vibrations detected. The increasing intensity can be explained by a shift into a resonance condition on which the system is aligned, because the signal is initially maximized for the relaxed  $S_2$  at an actinic pump delay of 1 ps.

Pump-DFWM measurements performed using a 430 nm actinic pulse are presented in Figure S10. The same vibrational features are present as when 420 nm excitation is employed,

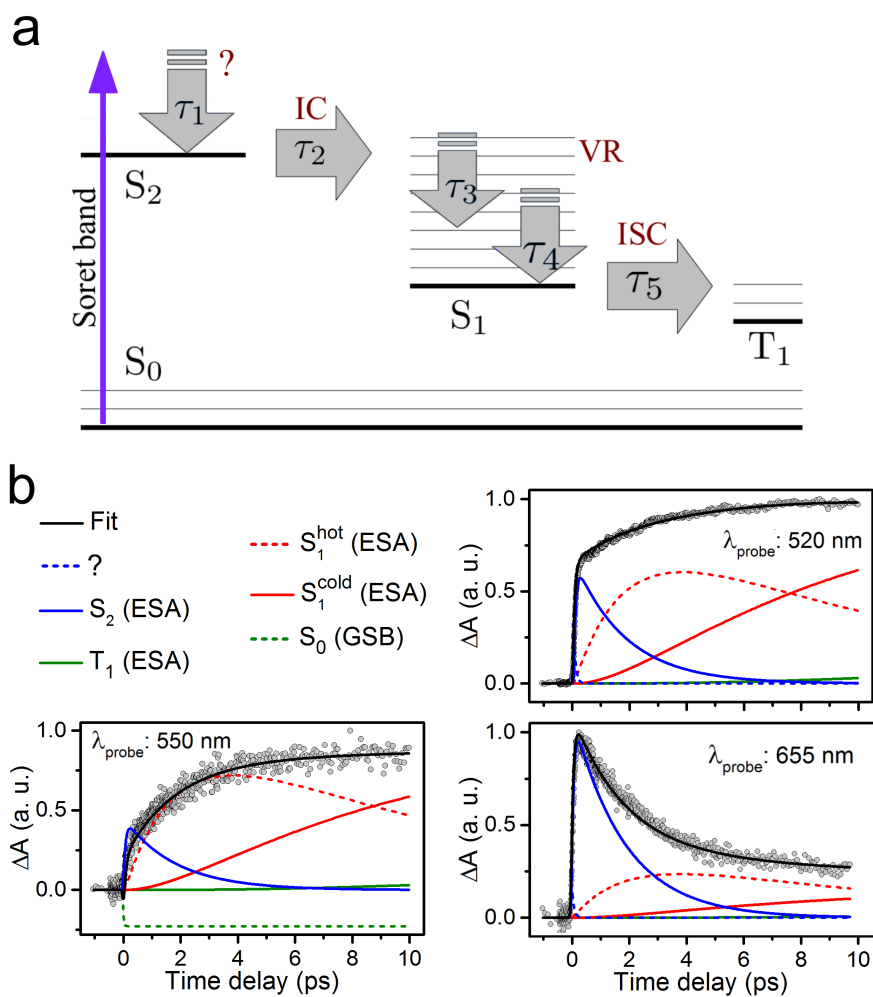


Figure S6: The dynamics of Soret-excited Zn-TPP involves five relaxation processes (a). Transient absorption signals from Zn-TPP solution detected at 520 nm, 550 nm, and 650 nm after 420 nm excitation and the contributions from each state (b) are found to include a fast 70 fs relaxation process.

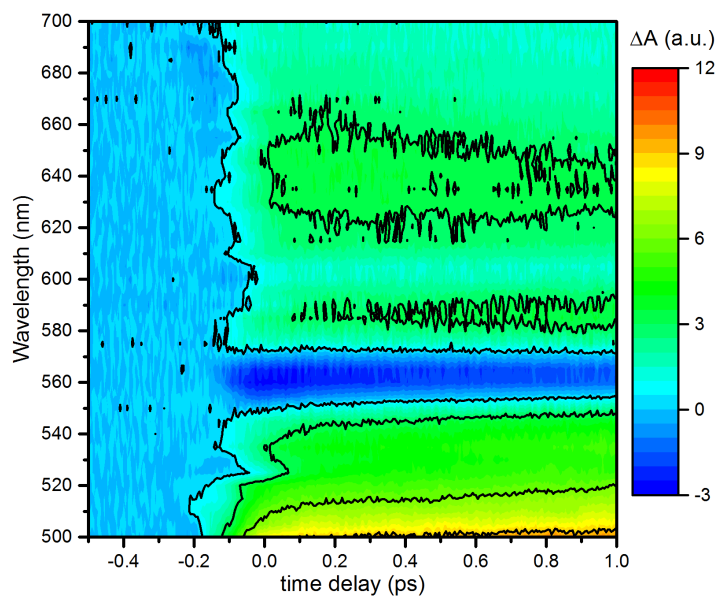


Figure S7: Transient absorption map of Zn-TPP after excitation at 430 nm.

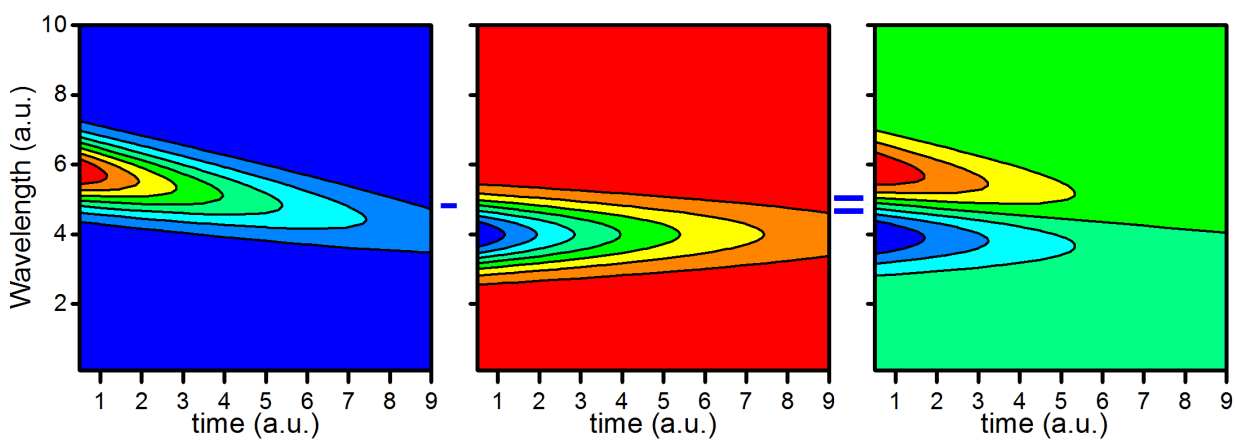


Figure S8: A simple simulation of a spectrally shifting hot state (left) and stationary cold state (middle) and their difference (right) produces a shift in the crossing point of zero intensity in the difference map.



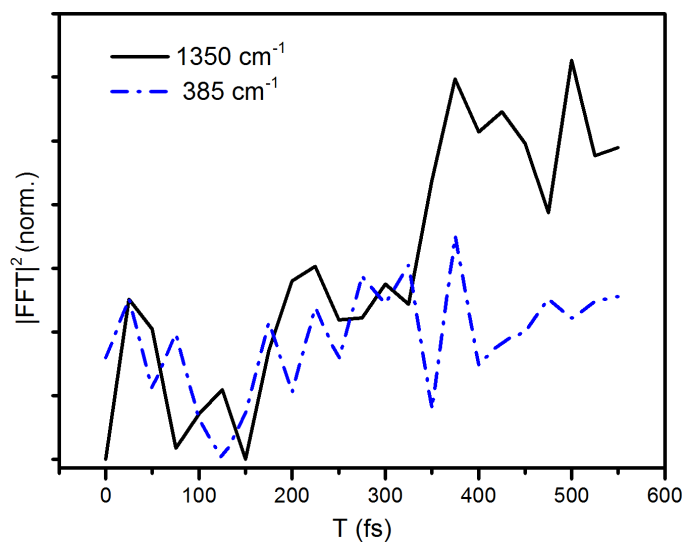


Figure S9: FFT peak intensity as a function of actinic pump delay for the two major vibrations shows a 250 fs rise of the higher frequency mode, inevent at the lower frequency.

however their time-dependence differs. Because the the lower energy 430 nm pump does not generate a vibrationally hot excited state and no frequency shifts are observed. The spectrum retains its shape over the inital 600 fs of dynamics.

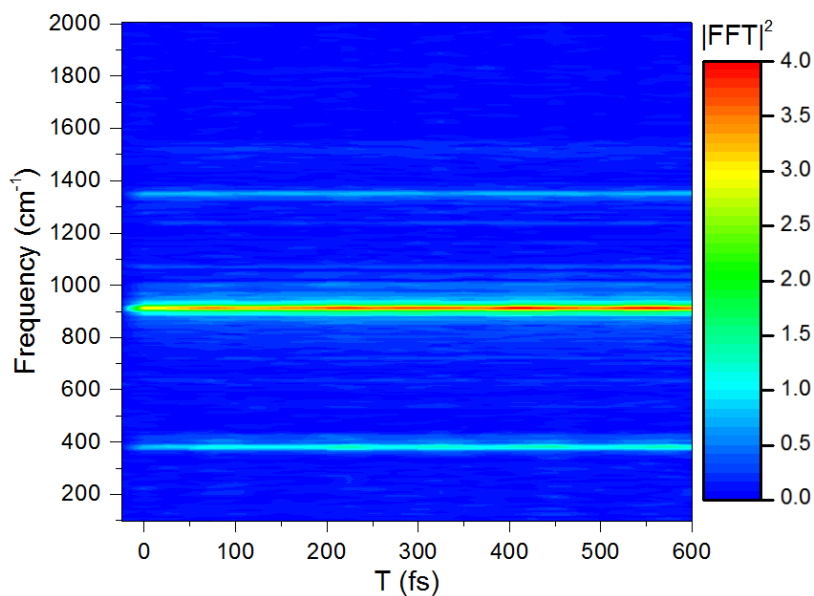


Figure S10: 430 nm excitation, on the red side of the  $S_0 \rightarrow S_2$  absorption maximum, produces an excited state vibrational spectrum that is unchanging during early dynamics.

## References

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