Evidence for the Two-State-Two-Mode Model in Retinal Protonated Schiff-Bases from Pump Degenerate-Four-Wave-Mixing Experiments

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Supplementary Information

Pump-DFWM experiments on Rhodamin B in Methanol

The following results demonstrate that vibrational coherences can be generated on arbitrary timescales from a relaxed excited-state population during the excited-state lifetime of large chromophores that do not undergo severe structural changes from ground- to excited electronic state equilibrium geometries. For this purpose, a structurally rigid Rhodamin B chromophore in methanol solution was chosen as an example. For this class of molecules ground- and excited state potential energy surfaces can be well described by harmonic potentials.[1] Analogous effects are observed in pump-DFWM experiments for a series of other structurally different laser dyes (not shown). Figure S1 a) shows example transients along the probe-direction (τ_{23}) from the pump-DFWM data of Rhodamin B at IP-delays of 790 fs (black) and 24,93 ps (red) after excitation at 500 nm and detection at 590 nm in spectral regions of excited state stimulated emission (ESE). The inset shows the calculated FFT-spectra of the oscillatory residuals after subtraction of an exponential fit to the population dynamics. For both delays, very similar sets of vibrational modes are clearly observable out of which we focus on the intense 625 cm^{-1} mode in the following. Figure S1 b) shows the dependence of the FFT-amplitude of the 625 cm^{-1} mode against IP-delay for two different timescales of measurements, i.e. during the initial few hundred femtoseconds after excitation (< 1 ps) as well as on timescales on which the excited state population can be regarded as completely relaxed (open circles). Note that vibrational dephasing and excited state population decay for Rhodamin dyes take place on timescales of a few picoseconds and several nanoseconds, respectively.[1-2] The following observations are of principle importance for the interpretation of the pump-DFWM results on RPSB (Figures 3-5 in the manuscript). Firstly, the FFT-amplitude of the well-known mode at 625 cm^{-1} corresponding to the ring-deformation motion in rhodamin-dyes[3] is modulated oscillatorily with a period corresponding to the vibrational period of the molecular motion (~ 53 fs) during the initial few picoseconds after IP-excitation ($T \approx 2$ ps). Secondly, the observed FFT-amplitude converges to an approximately constant, non-negligible value during the timescale of our experiment after the initially excited vibrational coherence has decayed ($T > 20$ ps). The observations clearly demonstrate that (i) vibrational coherences can be excited from two possible pathways by the DFWM-sequence, i.e., out of a relaxed excited state population (non-oscillatory contribution) as well as persisting vibrational coherence (oscillatory contribution); and (ii) after the initial coherence has decayed, only the contribution originating from the stationary population determines the FFT-amplitude. The origin of the oscillatory modulation has been verified by positively chirping the IP-pulse pulse to ~ 90 fs with glass-substrates. Such excitation conditions strongly diminish vibrational coherence contributions to the signal[4], while non-oscillatory contributions originating from population dynamics are still persistent (Figure S2 b), filled circles). The observations can be explained by non-time-dependent Franck-Condon factors for the corresponding vibrational mode during the excited state relaxation as expected by experimentally observable close mirror-image symmetry of ground-state absorption and excited-state emission for Rhodamine-dyes.[1] Although we focus here on the vibrational mode at approximately 625cm^{-1} analogous observations hold for the other modes as well. In this regard, these results significantly differ from the observations made for RPSB.

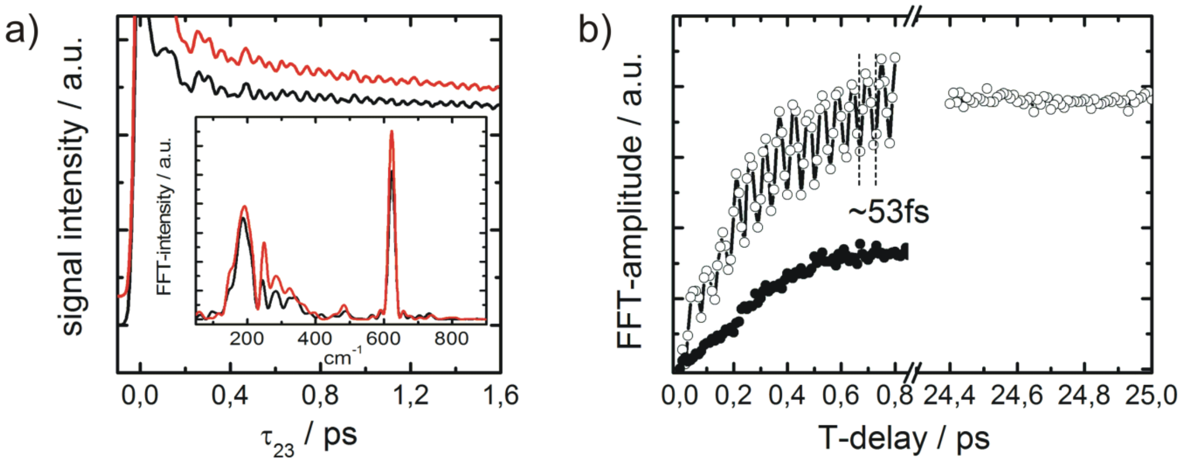

Figure S1. a) Pump-DFWM transients in direction of probe delay for IP-delays at 790 fs (black) and 24,93 ps (red). The inset shows the corresponding calculated FFT-spectra of the oscillatory residuals after subtraction of an exponential fit to the population dynamics. b) FFT-amplitude in dependence of IP-delay obtained from pump-DFWM data of Rhodamin B in methanol solution for near transform-limited excitation pulses (~ 20 fs, open circles) as well as strongly positively chirped excitation (~ 700 fs^2, filled circles). Excitation with the initial pump (IP) pulse was performed at 510 nm. The DFWM-sequence was tuned to the spectral region of excited-state stimulated emission (ESE, ~590 nm).

Pump-DFWM experiments on RPSB in Acetonitrile and Cyclohexane

In order to investigate the effect of solvent polarity on the initial relaxation dynamics of internal vibrational energy redistribution (IVR) in RPSB, pump-DFWM experiments in solvents of different dielectic properties (compared to ethanol, as a polar protic solvent, reported in the manuscript) have been performed. Acetonitrile (MeCN) was chosen as a polar, aprotic solvent of high static dielectic constant whereas cyclohexane (cHex) was chosen as an apolar, aprotic solvent with a low static dielectric constant.[5] Figure S2 together with Figure 5 in the manuscript demonstrate that solvent properties play a negligible role in the IVR process discussed in the manuscript for ethanol. Both, the oscillatory modulation of the FFT-amplitude as well as diminishing FFT-amplitudes indicative for time-dependent FC-factors are clearly identified in all solvents on indistinguishable timescales. This is completely in line with earlier experimental findings regarding vibrational dynamics in excited states of RPSB which indicated only minor effects of solvent properties.[6]

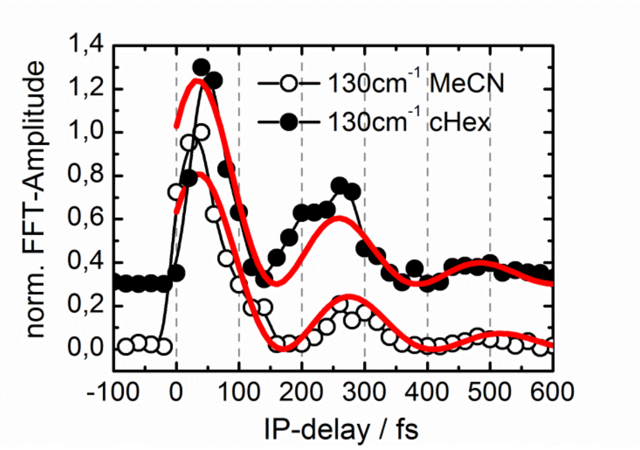

Figure S2. Normalized FFT-amplitudes at 130 cm^{-1} (black filled and open circles) for pump-DFWM measurements on RPSB dissolved in acetonitrile (MeCN, open circles) and cyclohexane (filled circles) both averaged over +/-15 cm^{-1} from central frequency detected at 580 nm. For clarity, the cyclohexane data are shown with an offset of 0.3. The red lines are oscillatory fits to the data intended to guide the eye with periods of 240 fs corresponding to the 130 cm^{-1} mode of RPSB.

References

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