Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Photo-Induced Oxidation of the Uniquely Liganded Heme *f* in the Cytochrome b_6f Complex of Oxygenic Photosynthesis.

Supplementary Information

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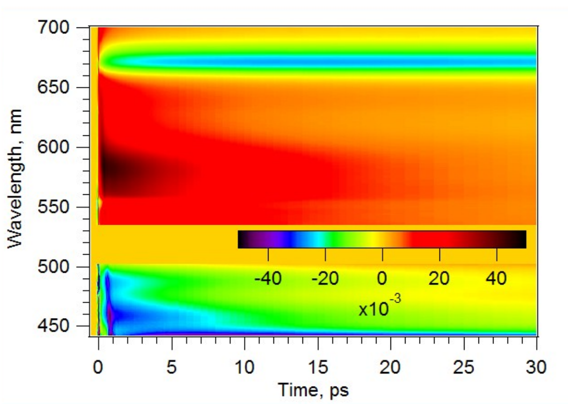
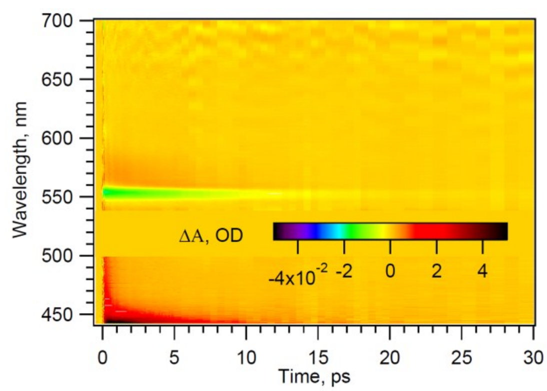
Heme *f* signal extraction.

The transient signal is dominated by the carotene (Car) S_1 and the chlorophyll *a* (Chl *a*) Q_y signals maximizing at 580 and 670 nm, respectively, as shown in Figure S1.



A.



B.

Figure S1: A. Raw transient surface data of the cyt b6f complex when the heme f is reduced. B. Extracted heme f signal. The color scales represent the amplitude of the transient absorption, in units of optical density.

The Car and Chl *a* signals are taken as a constant background. The heme *f* signal is extracted by taking the difference between the raw data when then heme *f* is reduced and the raw data when the heme *f* is oxidized. The validity of the manipulation can be appreciated by the lack of residual signals from both Car and Chl *a*.

Fitting procedure of the heme f signal.

The heme *f* signal is assumed to be a superposition of a bleach (blue solid curve), characterized by the oxidized minus reduced spectrum, and a shift (green solid curve), characterized by the difference between the difference between the static heme f's reduced-oxidized spectrum (pink solid curve) and its shifted duplicate (purple solid curve), as represented in Figure S2. The fitting procedure was done using Matlab's minimizing function called "patternsearch" in order to avoid falling into local minimum.

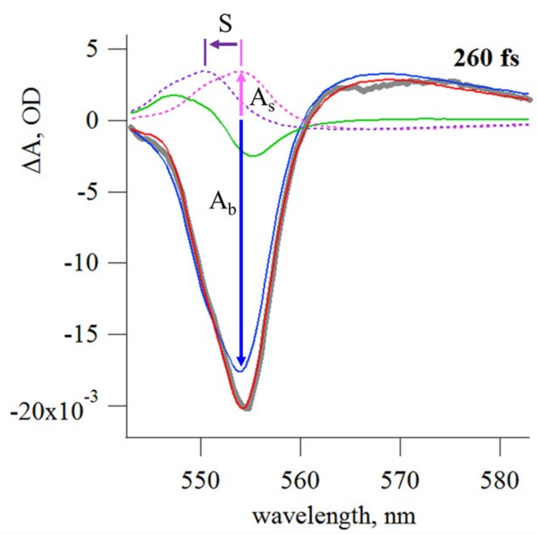


Figure S2: Visual representation of the fitting parameters

The time evolution of the different fitting parameters is plotted in Figure S 3.

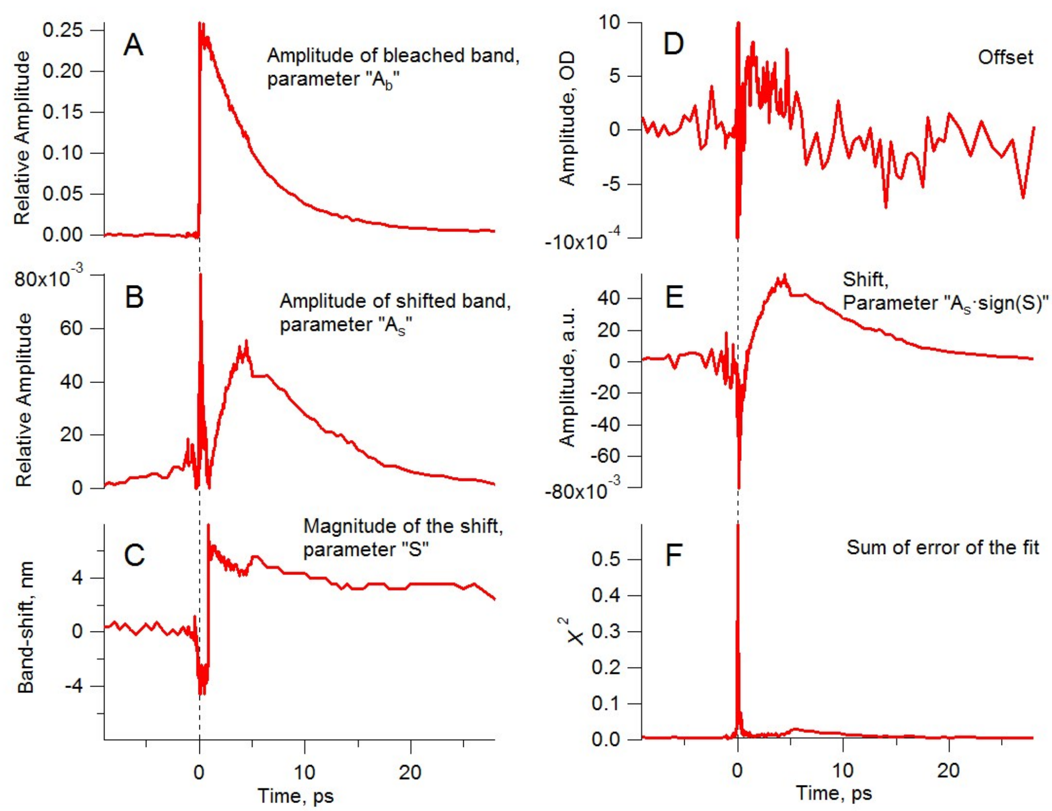
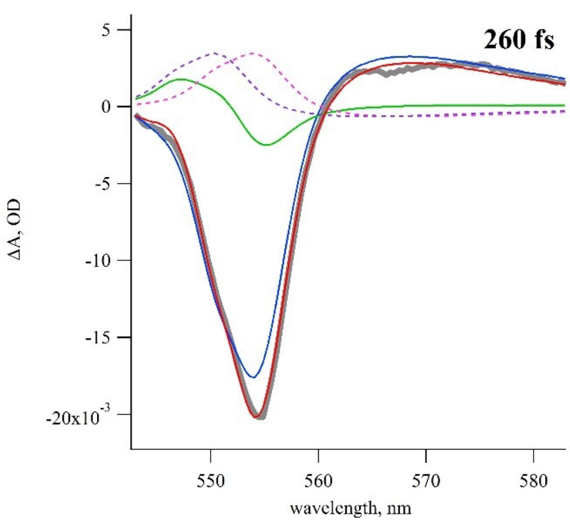


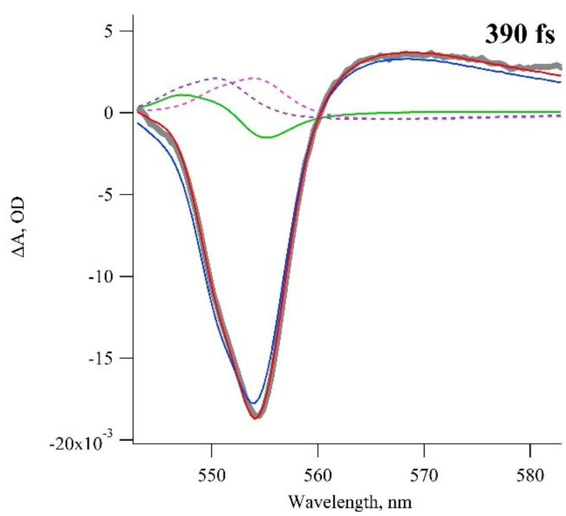
Figure S 3: Time evolution of the fitting parameter. Panel A shows the amplitude of the reduced minus oxidized heme f spectrum used for the reconstruction of the bleach, i.e. parameter "A_b", relative of the heme f static spectrum. Panel B show the amplitude of the reduced minus oxidized heme f spectrum used for the reconstruction of the shift, i.e. parameter "A_s", relative of the heme f static spectrum. Panel C shows the magnitude of the shift, i.e. parameter "S". Panel D shows the amplitude of the offset used in order to account for the background noise. Panel E shows the variable "A_s" multiplied by the sign of the shift "S". Panel F show the χ^2error function.

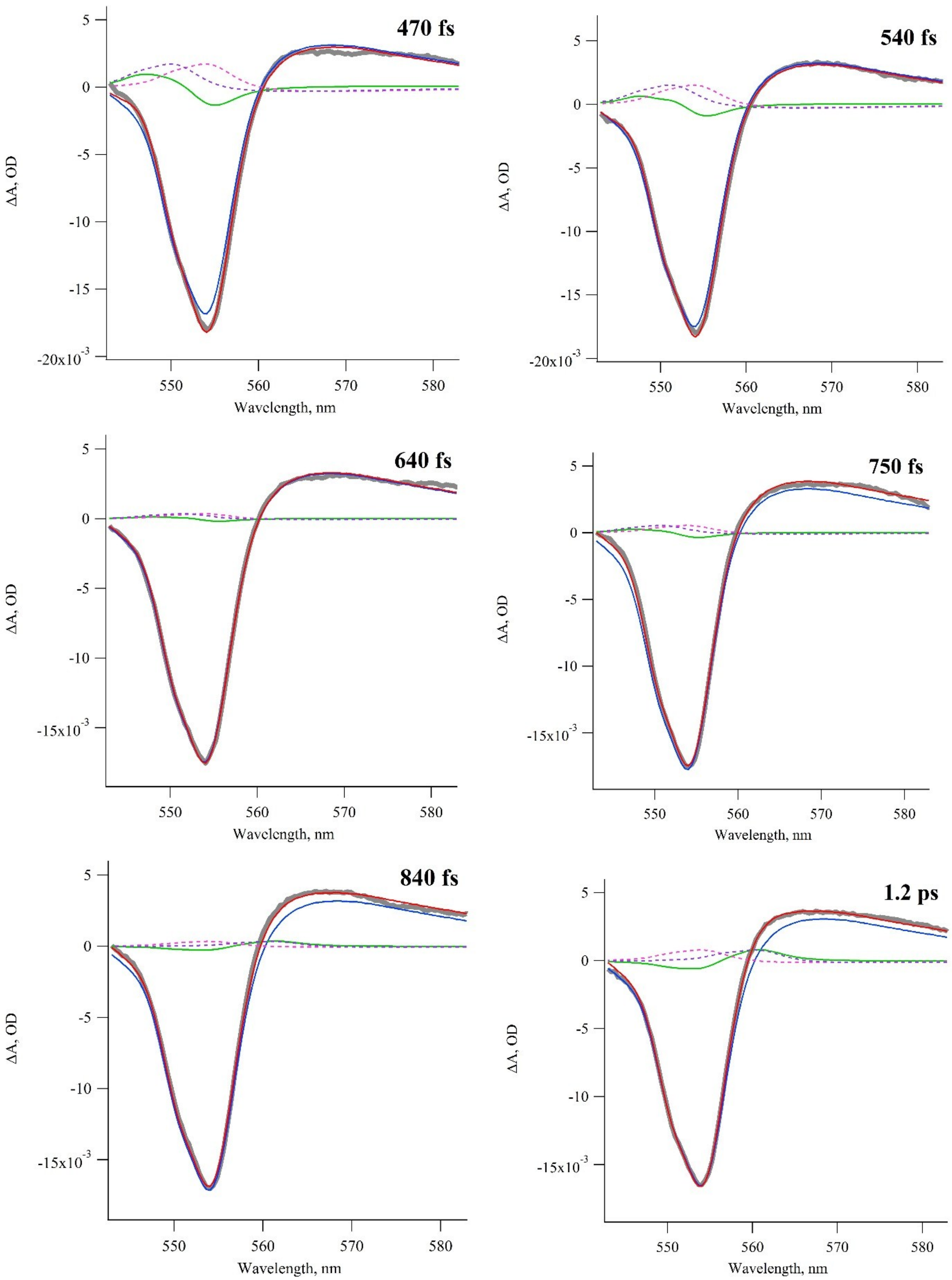
Note that the abrupt change and noise of the “S” parameter (Figure S 3, panel C) around 600 fs is due to the small amplitude of the shift (the “A_S” parameter, Figure S 3, panel B). A flat background is also added to compensate for any possible fluctuation due to light scattering (Figure S 3, panel D), but is only relevant at long time delays (> 20 ps) when the signal amplitude approaches the noise level. The fitting quality is finally assessed by means of χ^2 as calculated by the mean-square deviation of the fit from the monitored spectra (Figure S 3, panel F). Since the shift goes from blue to red, the curve representative of the shift’s amplitude has to be adjusted for this change of sign. The parameter “A_S” is then multiplied by the sign of the “S” parameter, as shown in (Figure S 3, panel E). The curves in panel A and E are further analyzed in the main manuscript.

Fitting results at selected time delays.

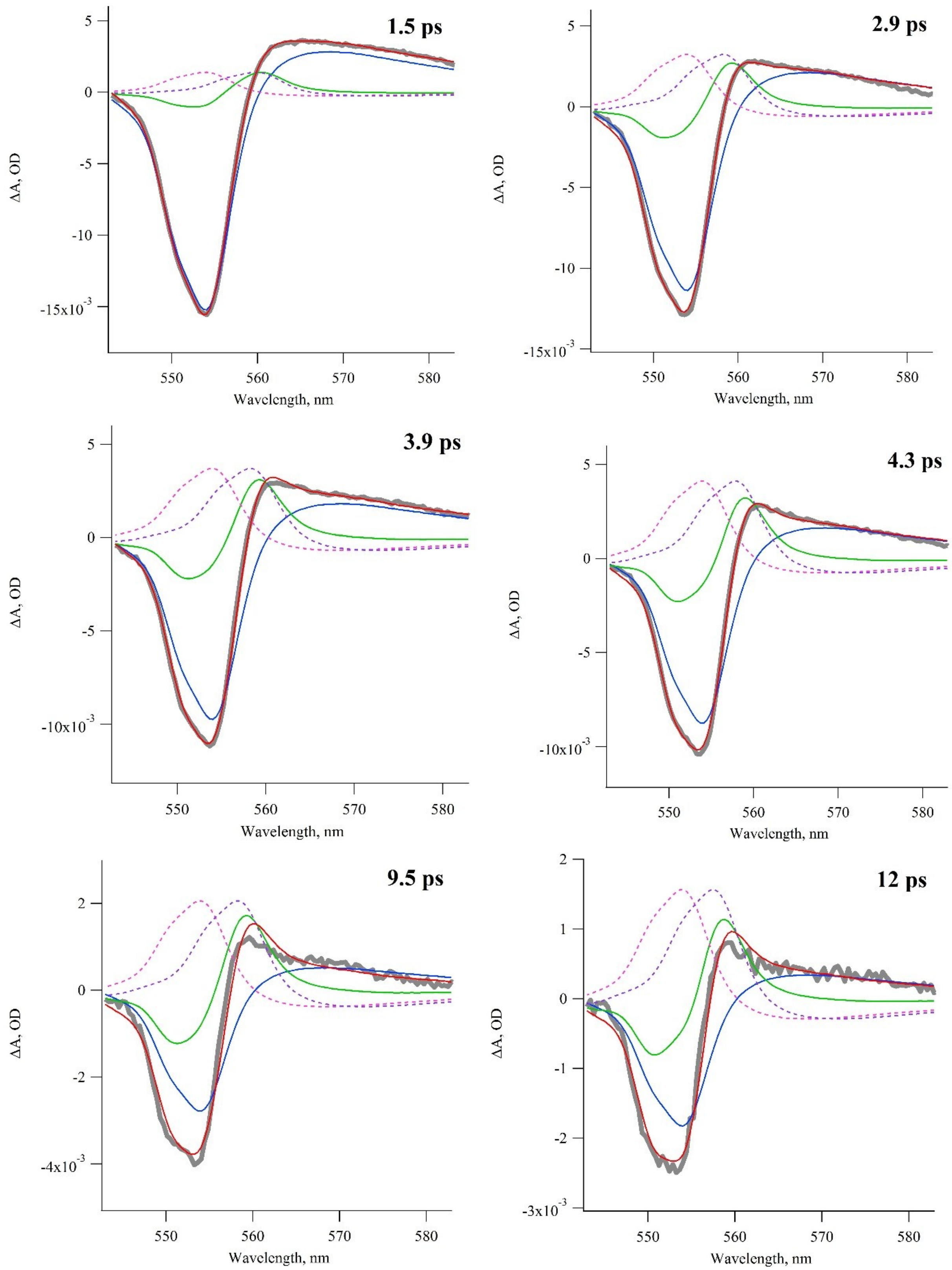
For all following spectra, in grey is the data, in red the fit, in blue and in green are the bleach and the shift contribution to the fit, respectively. The dashed pink and purple represent the initial and final (shifted) α-band contribution to the shift (green curve). We show only the fits of 18 spectra out of a total of the 270 time delays.



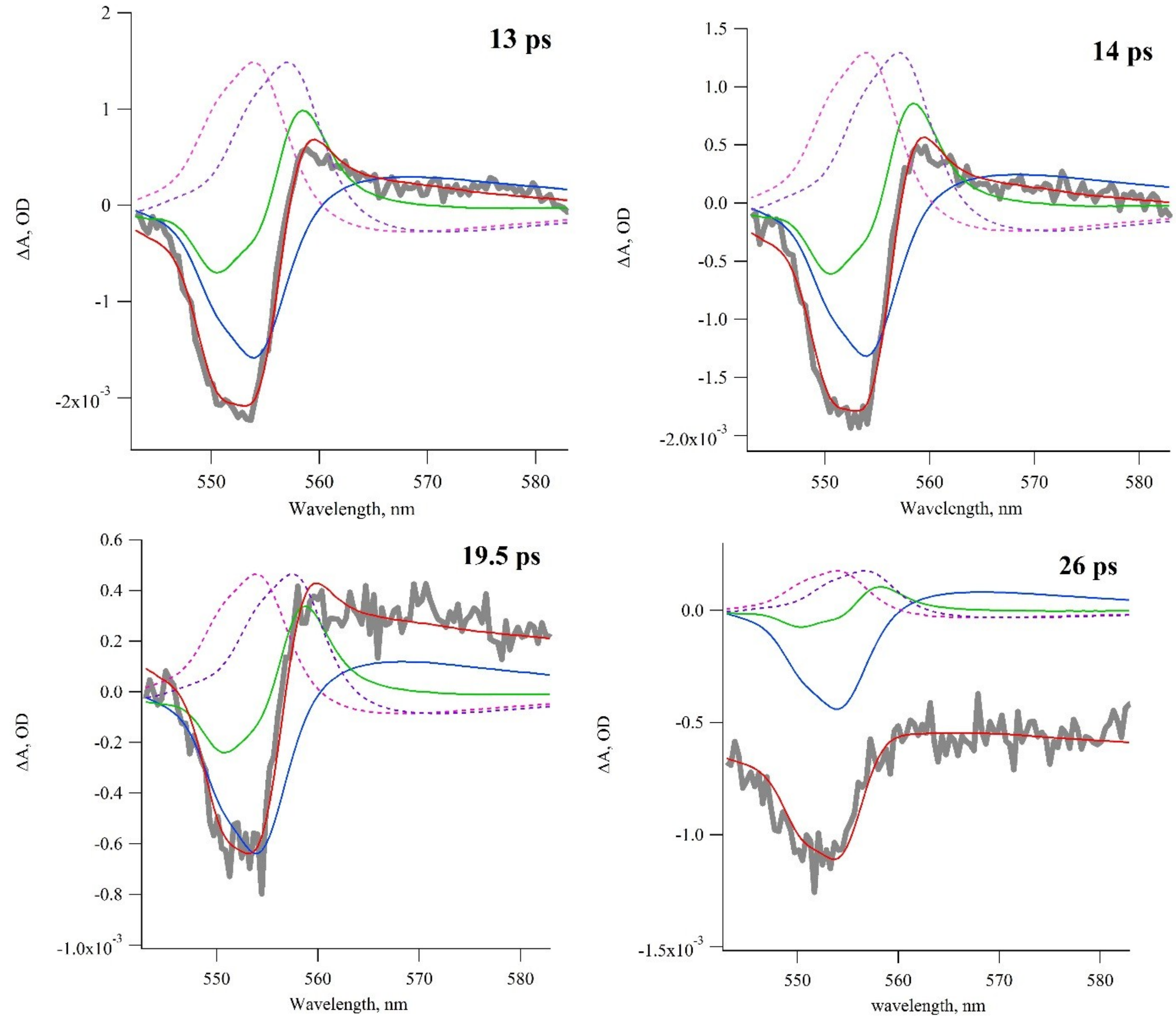




470 fs
540 fs
640 fs
750 fs
840 fs
1.2 ps
ΔA, OD
Wavelength, nm
-20x10^-3
-15x10^-3
-15
-10
-5
0
5
550
560
570
580



1.5 ps
2.9 ps
3.9 ps
4.3 ps
9.5 ps
12 ps
ΔA, OD
Wavelength, nm
-15x10^-3
-10x10^-3
-4x10^-3
-3x10^-3
550
560
570
580



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