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

Supplementary Information for Energy- and Conformer-Dependent Excited-State Relaxation of an E/Z Photoswitchable Thienyl-Ethene

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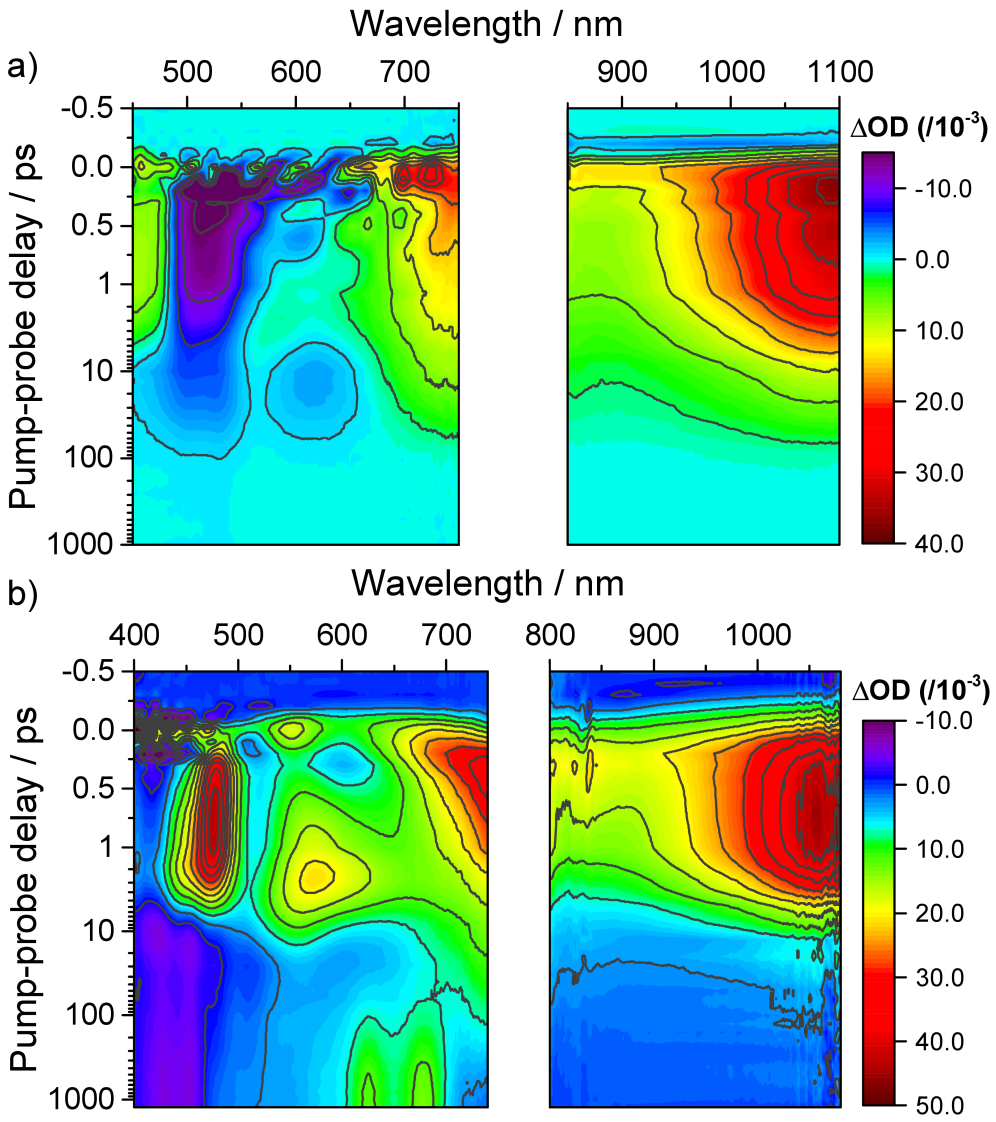


Figure S1: Contour plots of transient absorption spectra of cis-4TCE (**1**) collected with (a) low energy (530 nm) and (b) high energy (420 nm) excitation. Data are plotted with split linear-log time axes to highlight spectral dynamics that occur on multiple timescales.

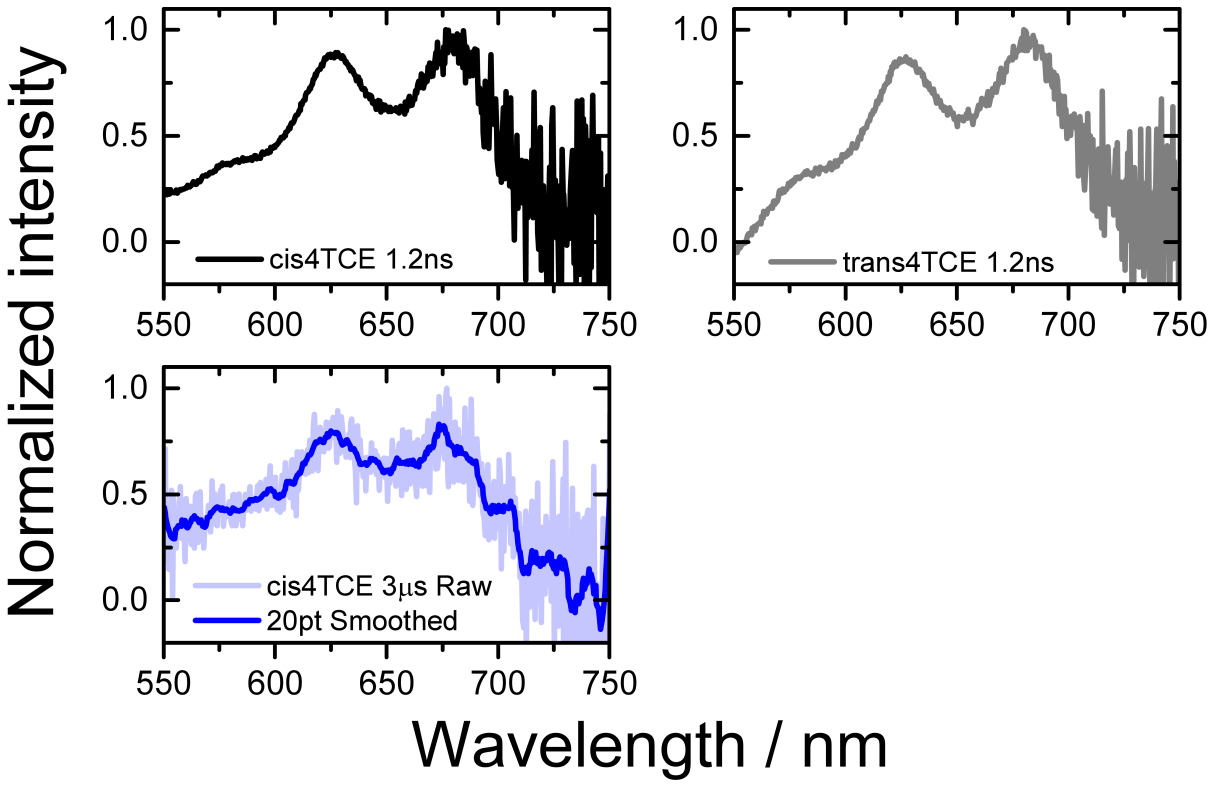


Figure S2. Comparison of triplet transient absorption spectra obtained for cis- and trans-4TCE (top left and right) collected at 1 ns and for cis-4TCE at 3 microseconds (bottom).

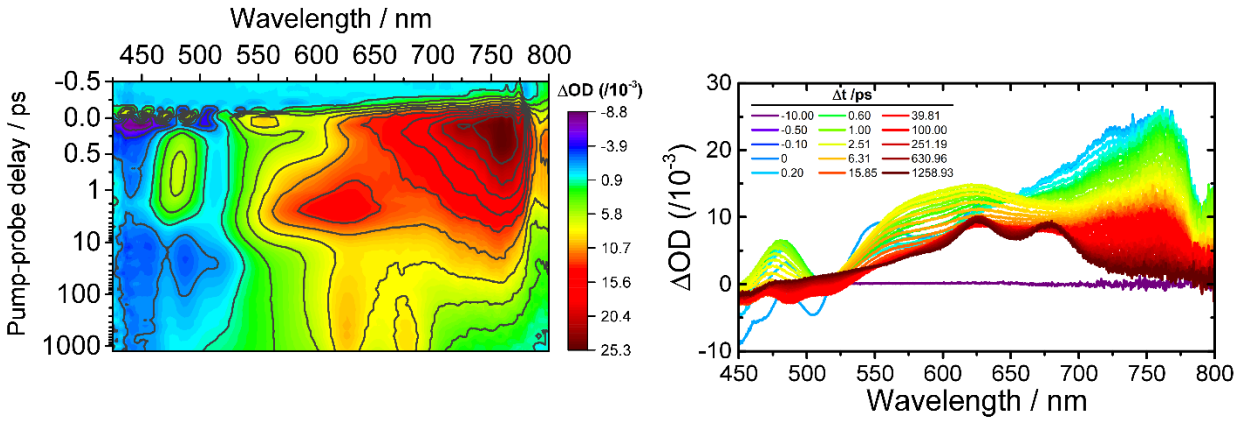


Figure S3. Transient absorption spectra collected with a cis-4TCE sample contaminated with a photooxidation product; plotted in contour and waterfall plots (left and right, respectively).

Note on the differences between data collected via 420-nm excitation of cis-4TCE in present and previous work

The most prominent difference between our previous and new data is the broad absorption band between 550 – 700 nm that overlaps significantly with both STA1 and SE and differs in spectral shape and evolution of STA3 in Figure 2(b). We previously assigned the appearance of this band to ultrafast population (~2 ps) and subsequent deactivation (~370 ps from global fitting) of a triplet state. However, comparison of triplet spectra collected at ~3 μs, utilizing microsecond TAS, with the spectrum seen at 1 ns in these most recent experiments, Figure S1, indicates that our initial assignment for this feature was incorrect: spectra collected recently for the lowest triplet states of the cis- and trans- isomers consistently exhibit significant vibronic structure, with features centered at 680 nm and 620 nm, that persists for the entire timescale probed in these experiments, >10 μs. Thus, we posit that the absorption features previously assigned to a triplet may actually be a feature associated with photoexcited contaminant in combination with STA3 and that the triplet state involved in the photophysics/photochemistry of cis-4TCE is actually populated on a ~200-300 ps timescale, as deduced from the analysis presented here. Additionally, we previously noted the presence of an isosbestic point at ~550 nm between the absorption of the putative cis-4TCE triplet and that of the trans isomer, indicative of isomerization within 1 ns after excitation; this may have rather corresponded with an isosbestic point associated with the relaxation of the photoexcited contaminant. In our new data a similar isosbestic point is not clear, and thus it appears that triplet cis-4TCE to ground-state trans-4TCE most likely does not occur within a nanosecond. Our previous triplet sensitization experiments support assignment of isomerization through the triplet manifold. Both photoinduced and sensitized isomerization most likely occur on the microseconds lifetime of the triplet state.

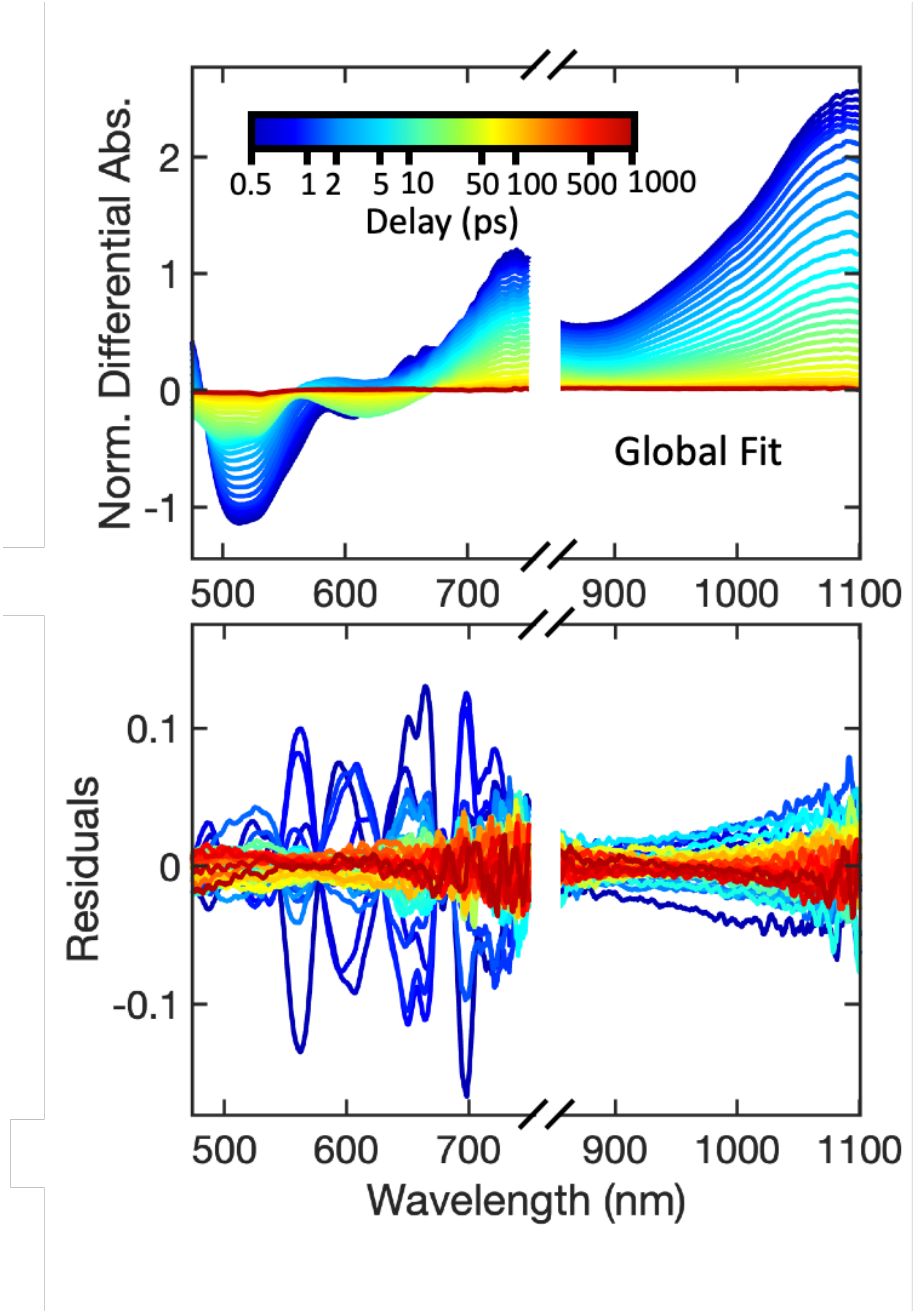


Figure S4. Global spectral fit (top) and residuals (bottom) for cis-4TCE TAS data collected with 530-nm excitation.

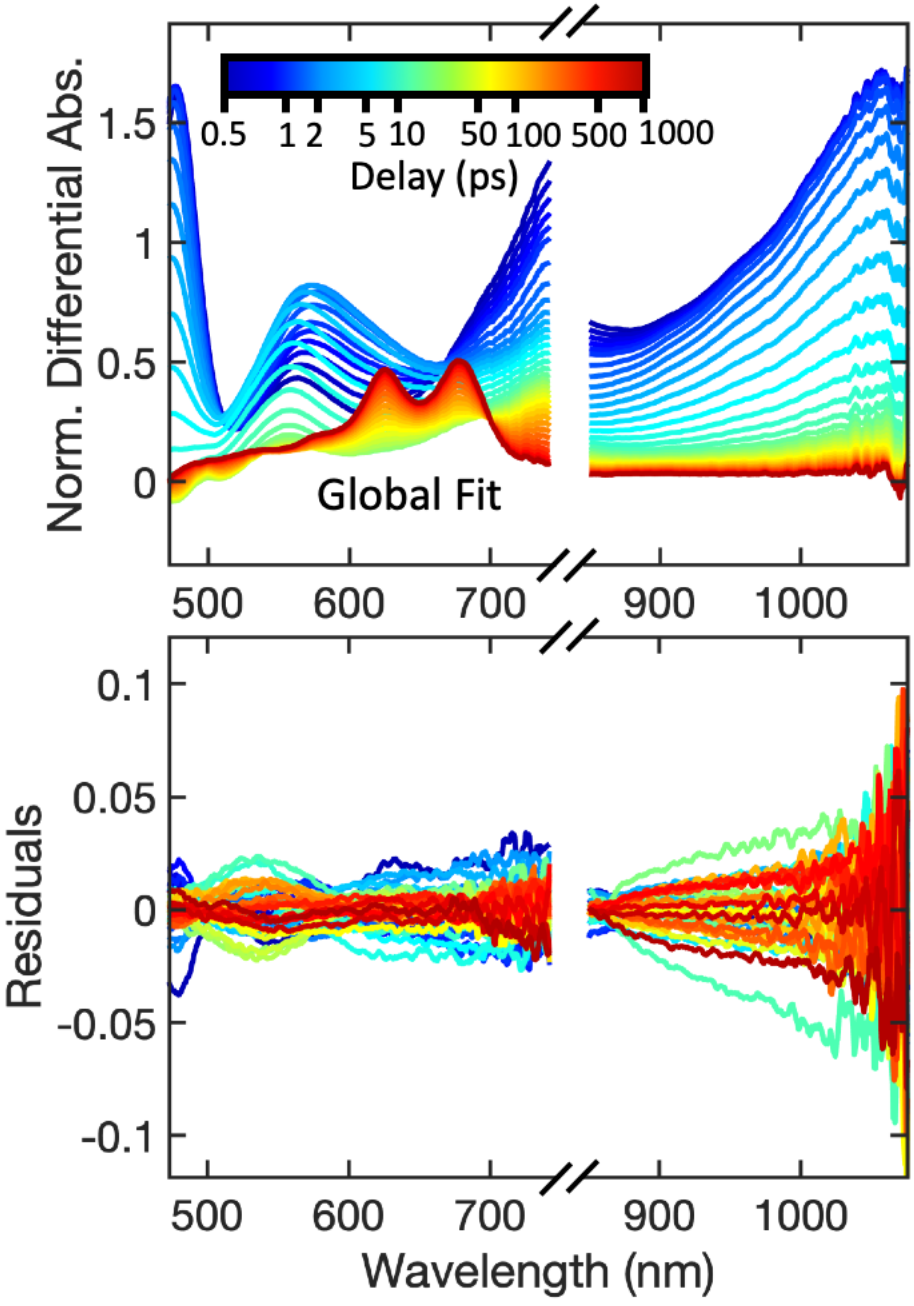


Figure S5. Global spectral fit (top) and residuals (bottom) for cis-4TCE TAS data collected with 420-nm excitation.

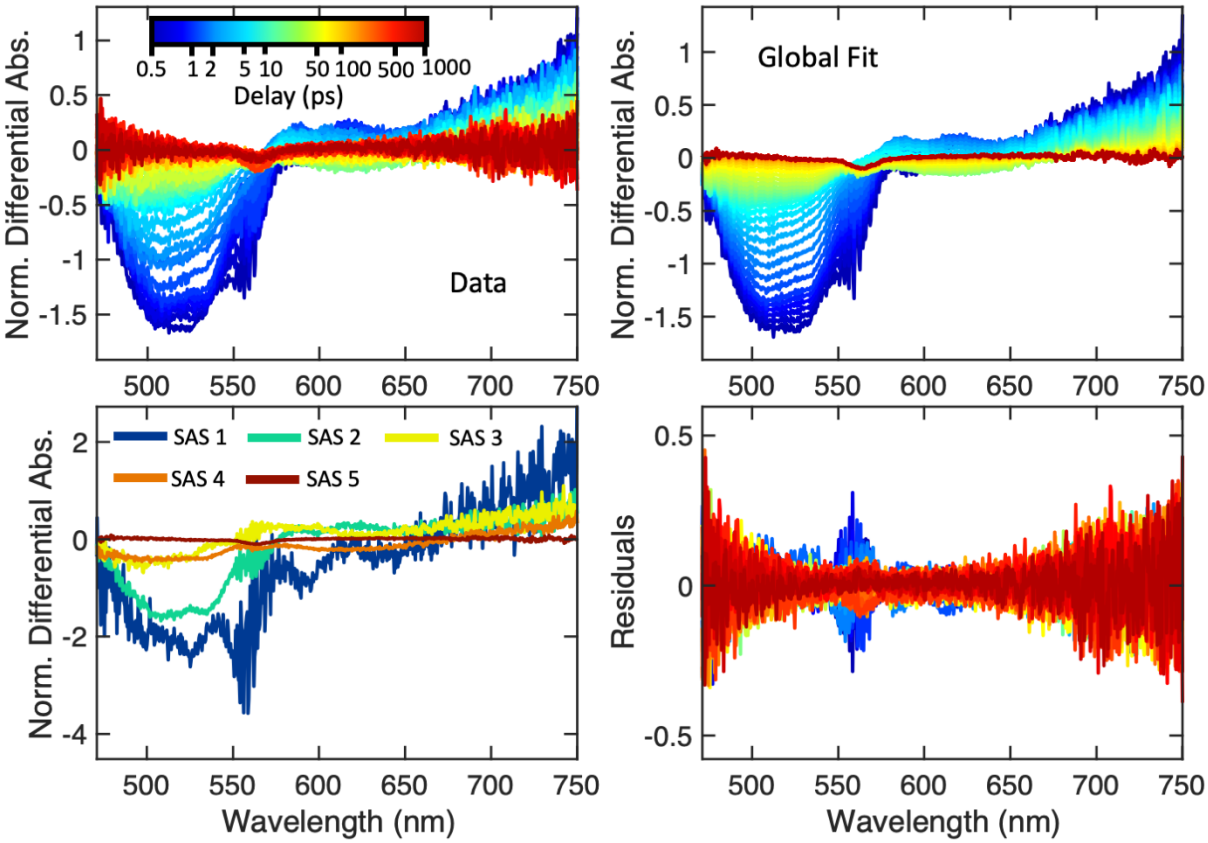


Figure S6. TAS of cis-4TCE excited at 565 nm: (top left) experimental data; (top right) global fit; (bottom left) species associated spectra; (bottom right) residuals. TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths.

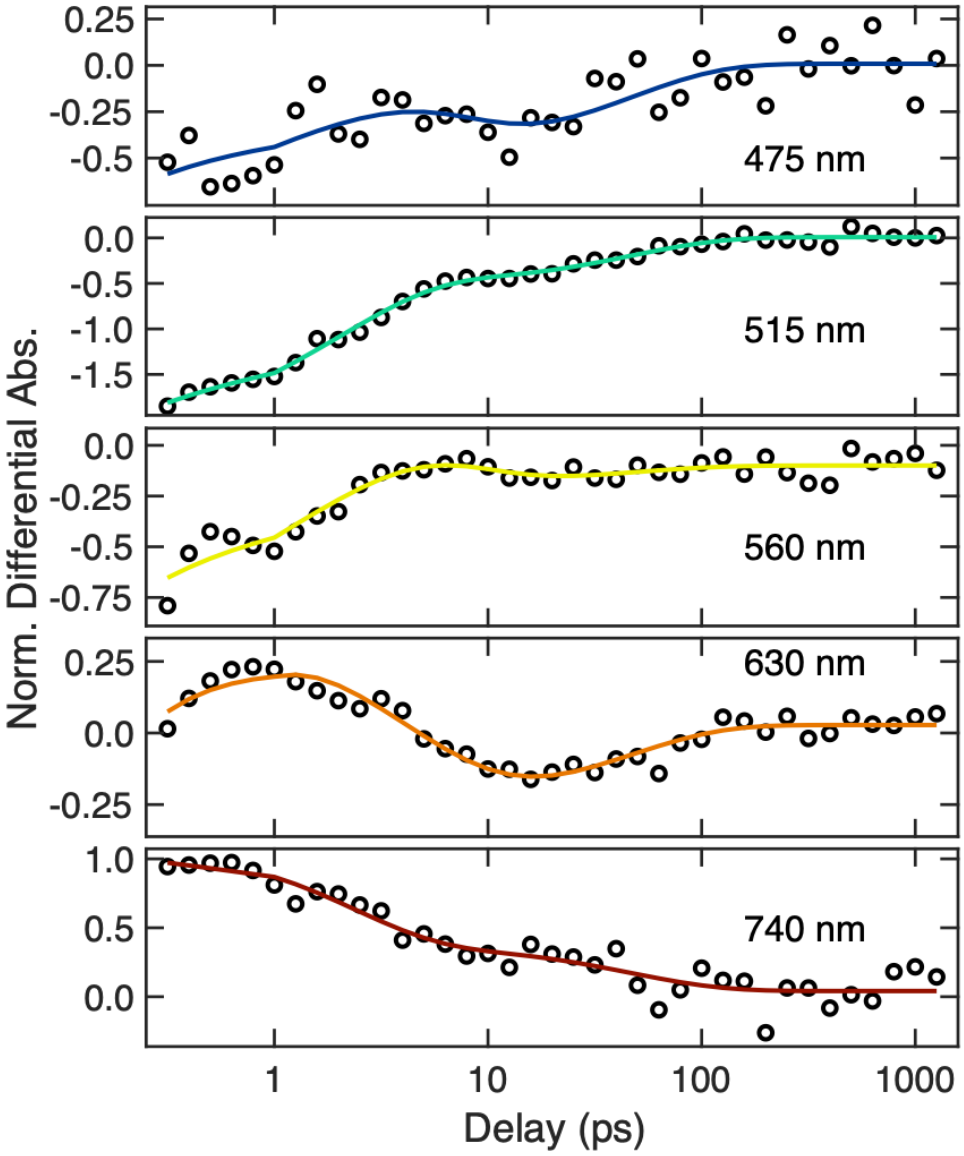


Figure S7. TAS of cis-4TCE excited at 565 nm: Time-dependent absorption at selected wavelengths (circles) with global fits (solid lines). TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths.

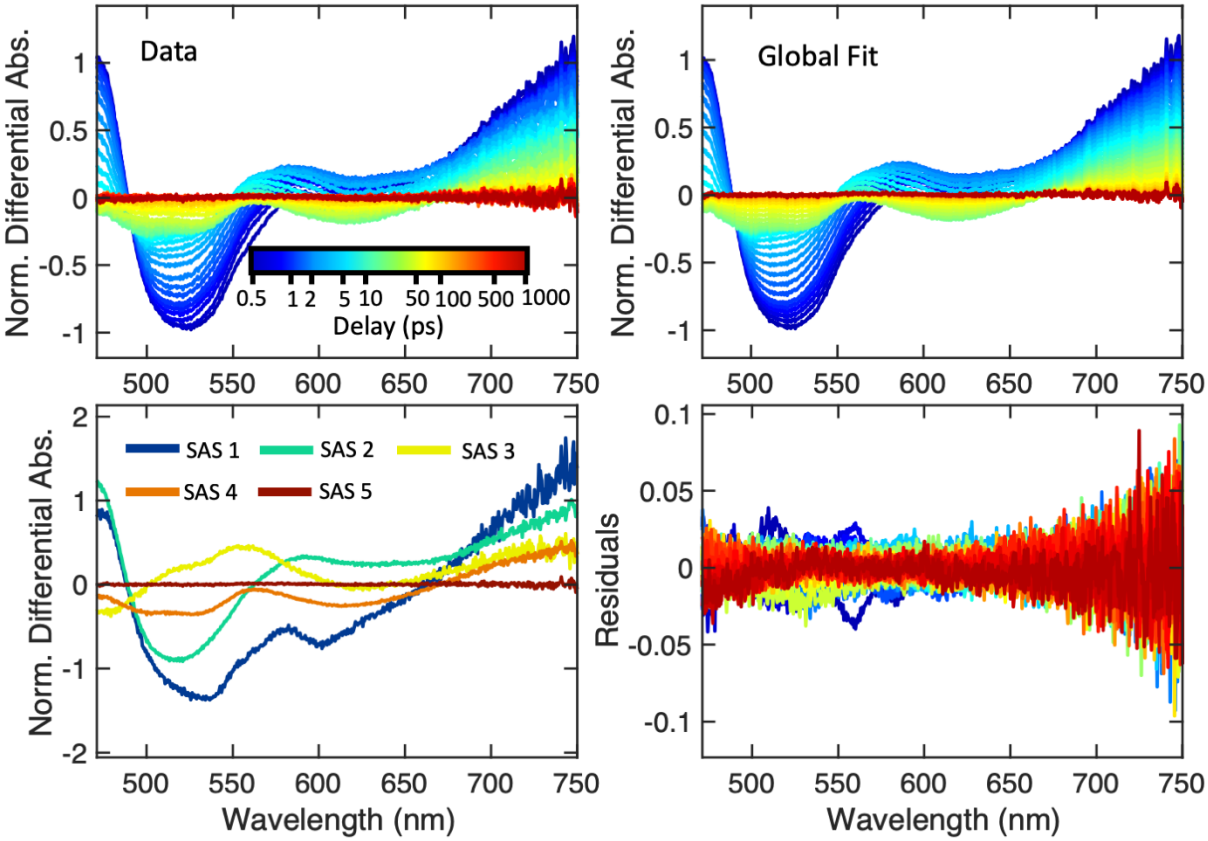


Figure S8. TAS of cis-4TCE excited at 520 nm: (top left) experimental data; (top right) global fit; (bottom left) species associated spectra; (bottom right) residuals. TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths.

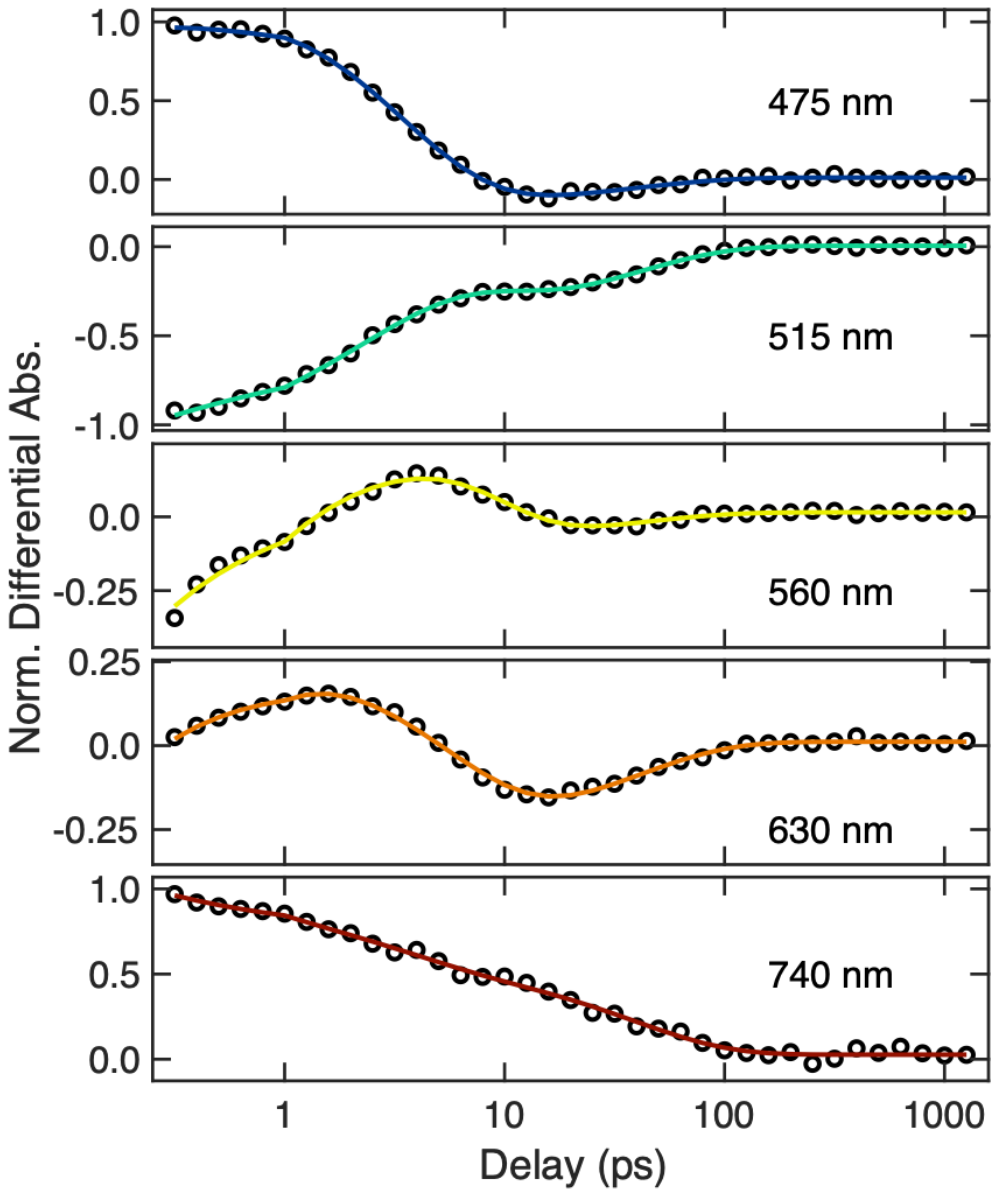


Figure S9. TAS of cis-4TCE excited at 520 nm: Time-dependent absorption at selected wavelengths (circles) with global fits (solid lines). TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths.

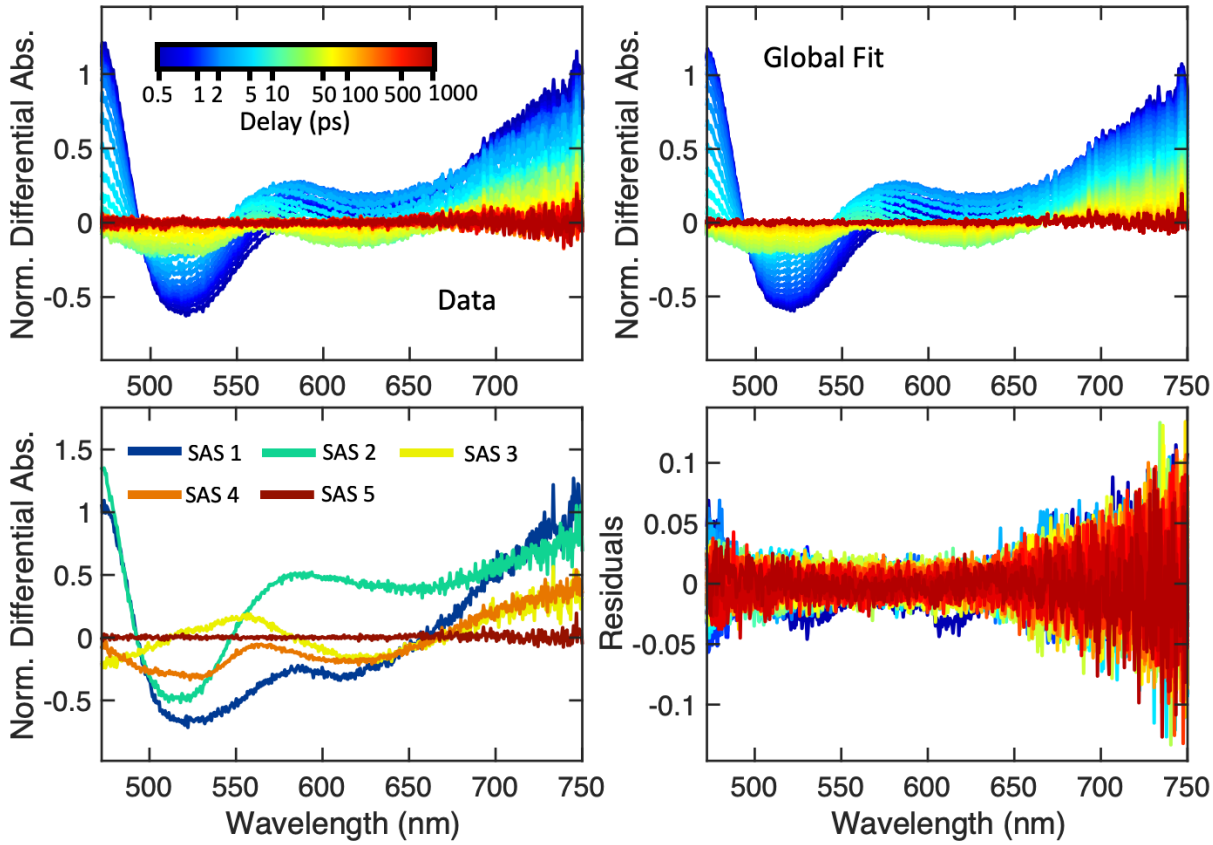


Figure S10. TAS of cis-4TCE excited at 510 nm: (top left) experimental data; (top right) global fit; (bottom left) species associated spectra; (bottom right) residuals. TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths

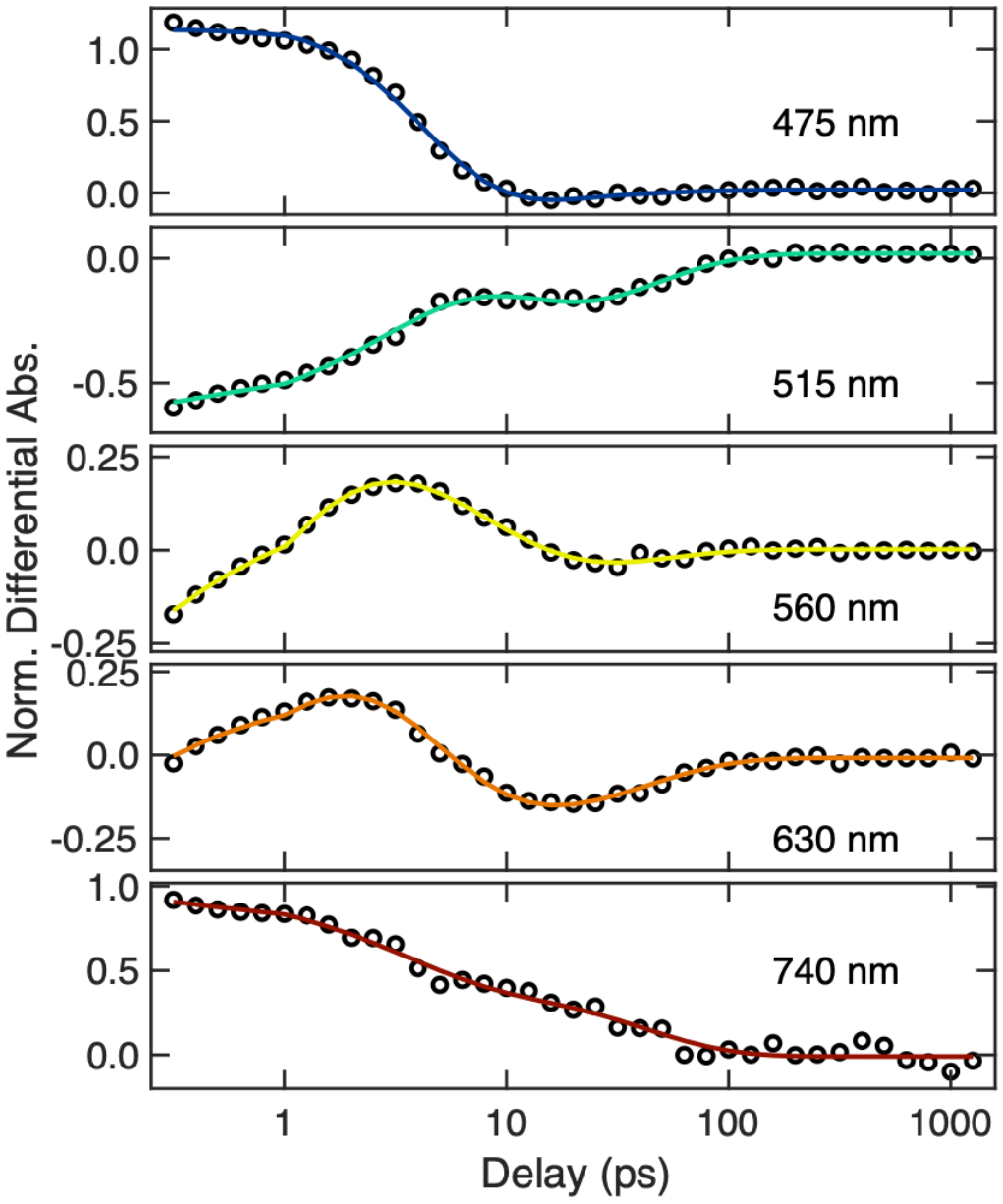


Figure S11. TAS of cis-4TCE excited at 510 nm: Time-dependent absorption at selected wavelengths (circles) with global fits (solid lines). TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths.

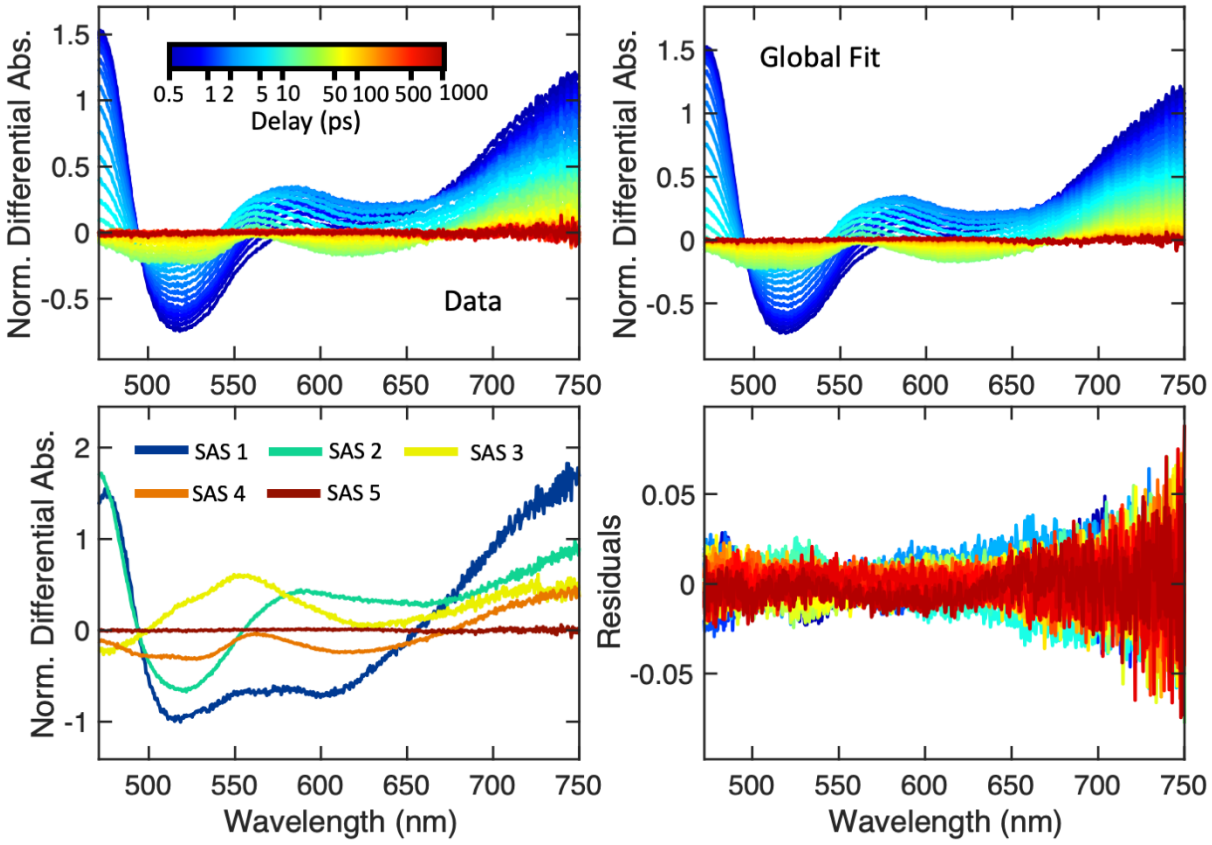


Figure S12. TAS of cis-4TCE excited at 500 nm: (top left) experimental data; (top right) global fit; (bottom left) species associated spectra; (bottom right) residuals. TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths

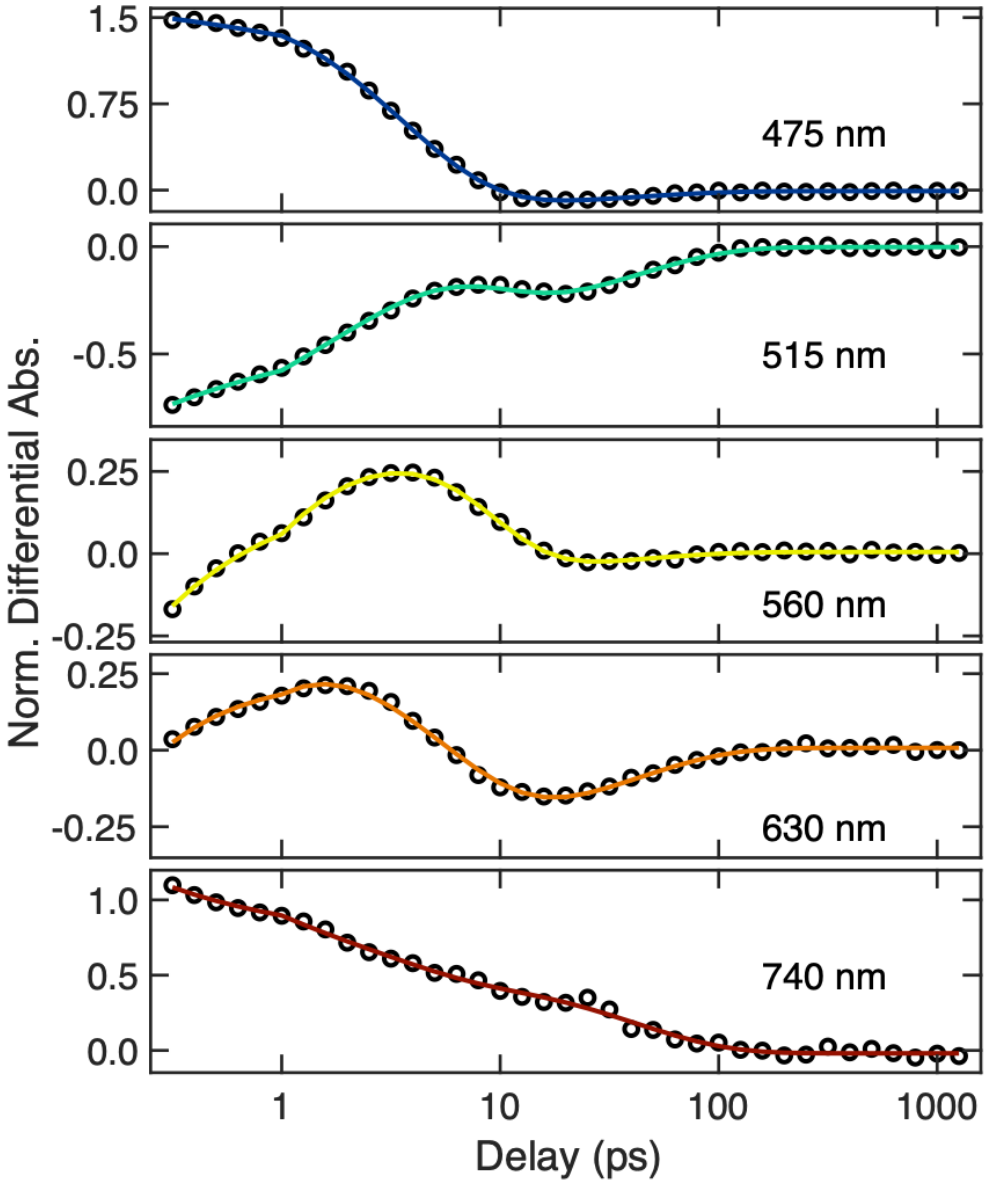


Figure S13. TAS of cis-4TCE excited at 500 nm: Time-dependent absorption at selected wavelengths (circles) with global fits (solid lines). TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths.

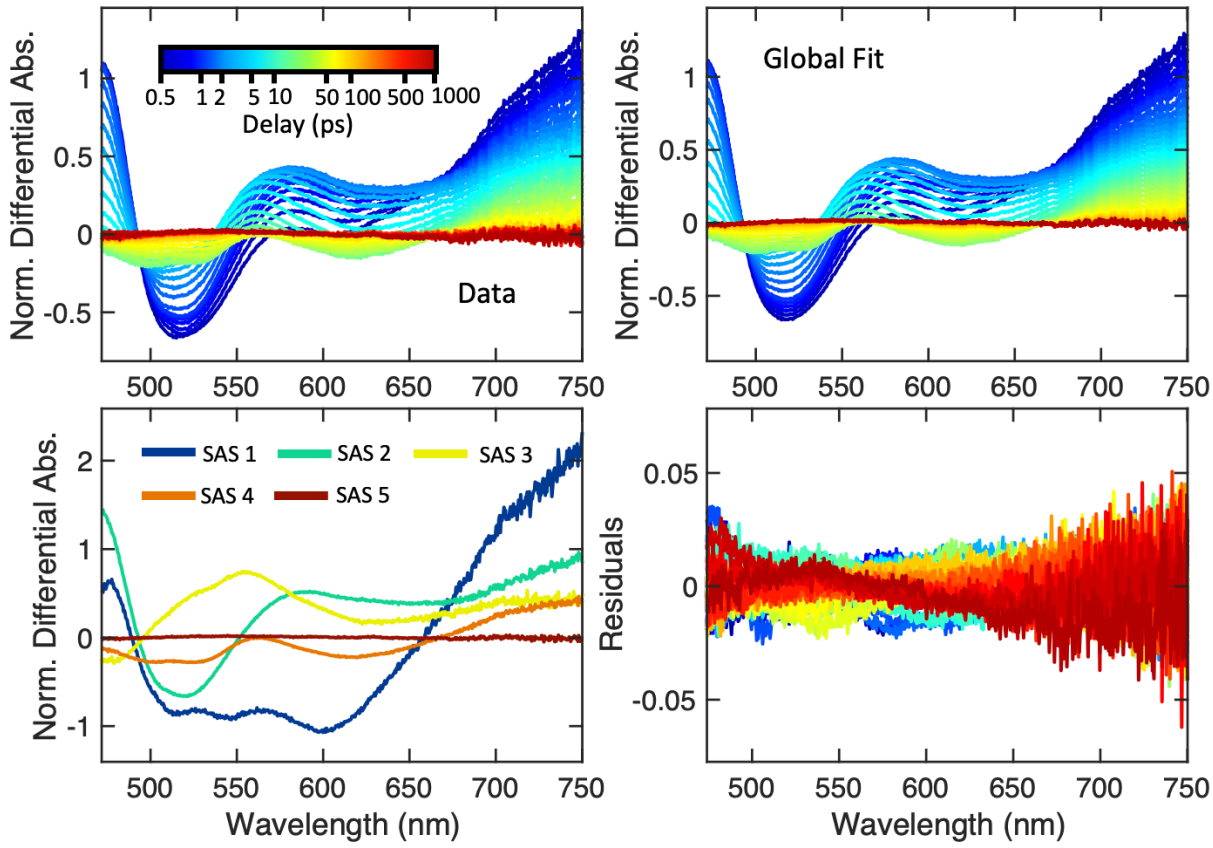


Figure S14. TAS of cis-4TCE excited at 490 nm: (top left) experimental data; (top right) global fit; (bottom left) species associated spectra; (bottom right) residuals. TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths

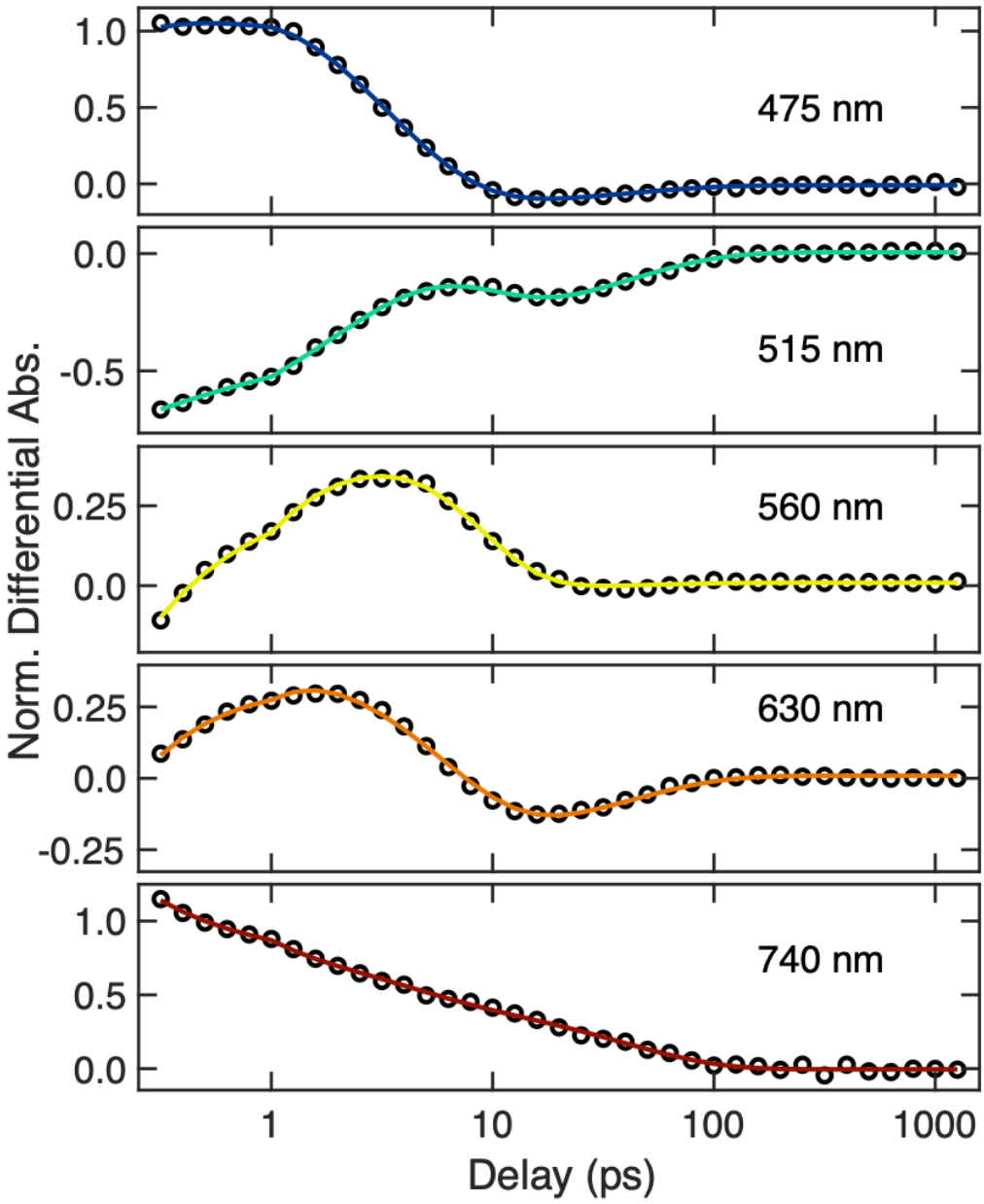


Figure S15. TAS of cis-4TCE excited at 490 nm: Time-dependent absorption at selected wavelengths (circles) with global fits (solid lines). TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths.

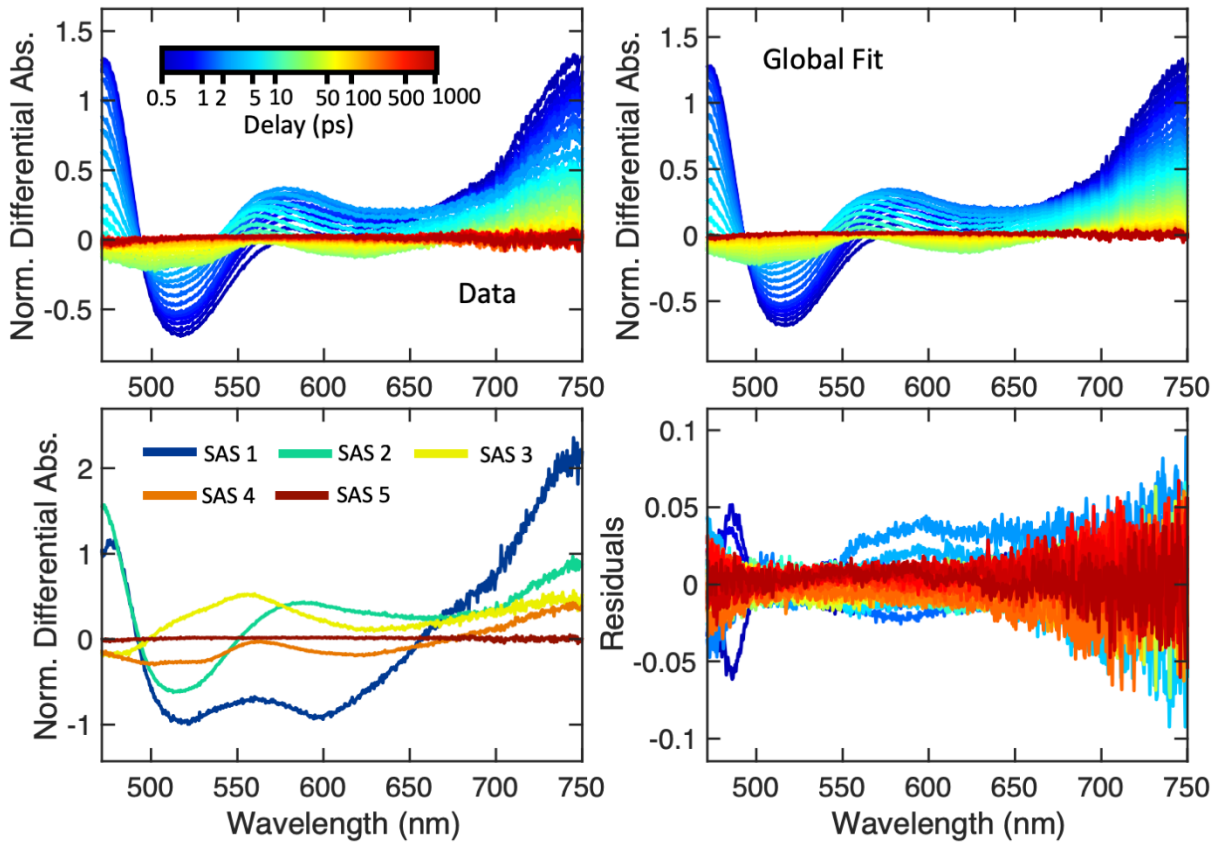


Figure S16. TAS of cis-4TCE excited at 485 nm: (top left) experimental data; (top right) global fit; (bottom left) species associated spectra; (bottom right) residuals. TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths

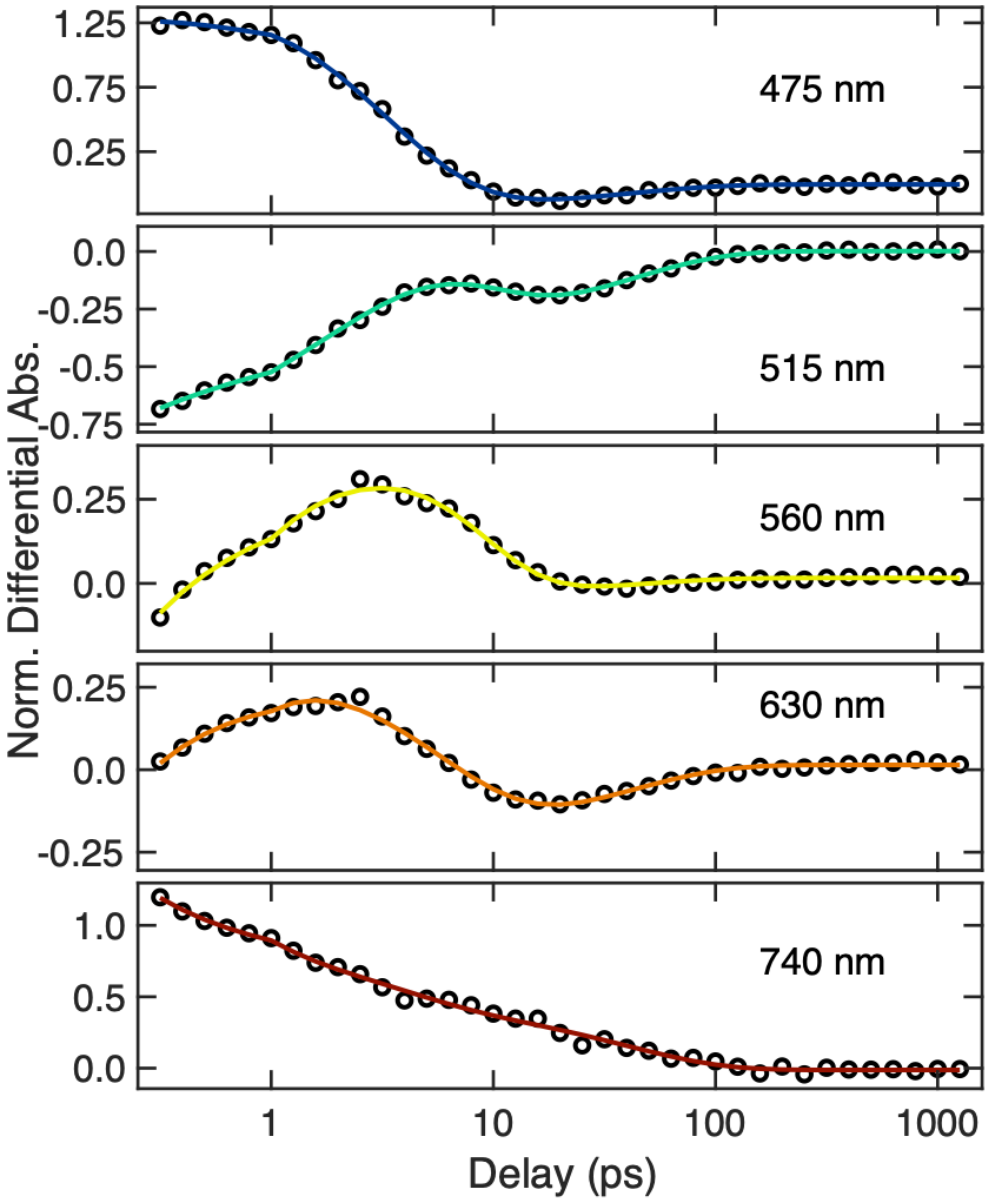


Figure S17. TAS of cis-4TCE excited at 485 nm: Time-dependent absorption at selected wavelengths (circles) with global fits (solid lines). TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths.

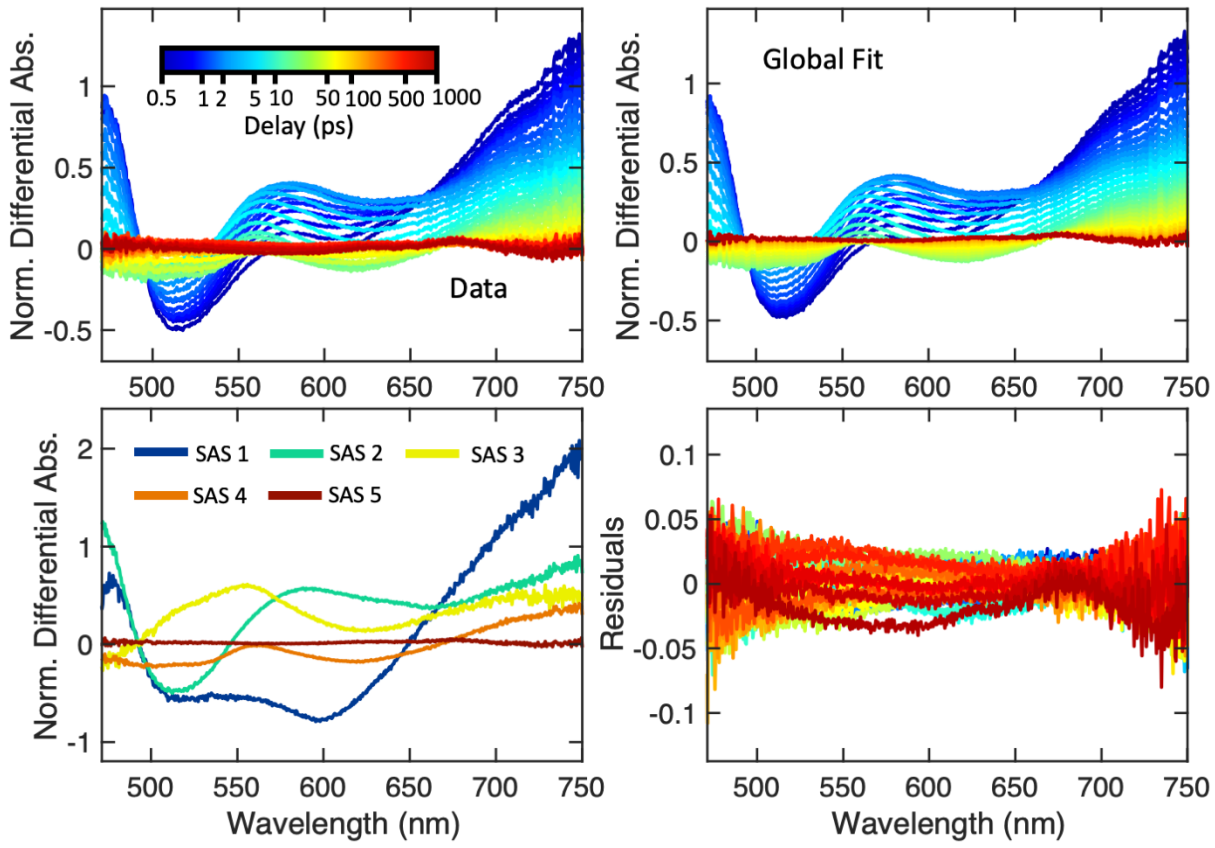


Figure S18. TAS of cis-4TCE excited at 480 nm: (top left) experimental data; (top right) global fit; (bottom left) species associated spectra; (bottom right) residuals. TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths

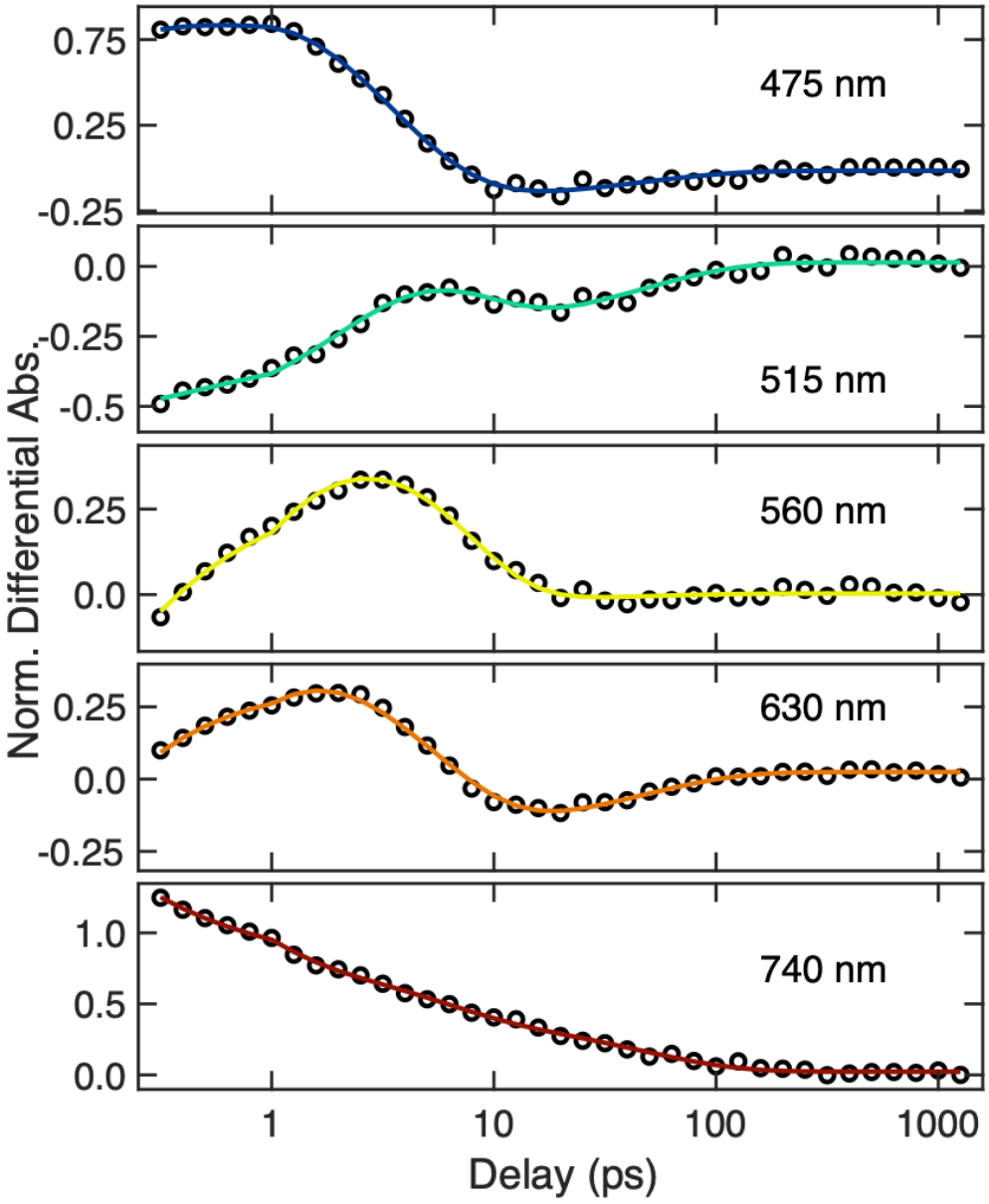


Figure S19. TAS of cis-4TCE excited at 480 nm: Time-dependent absorption at selected wavelengths (circles) with global fits (solid lines). TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths.

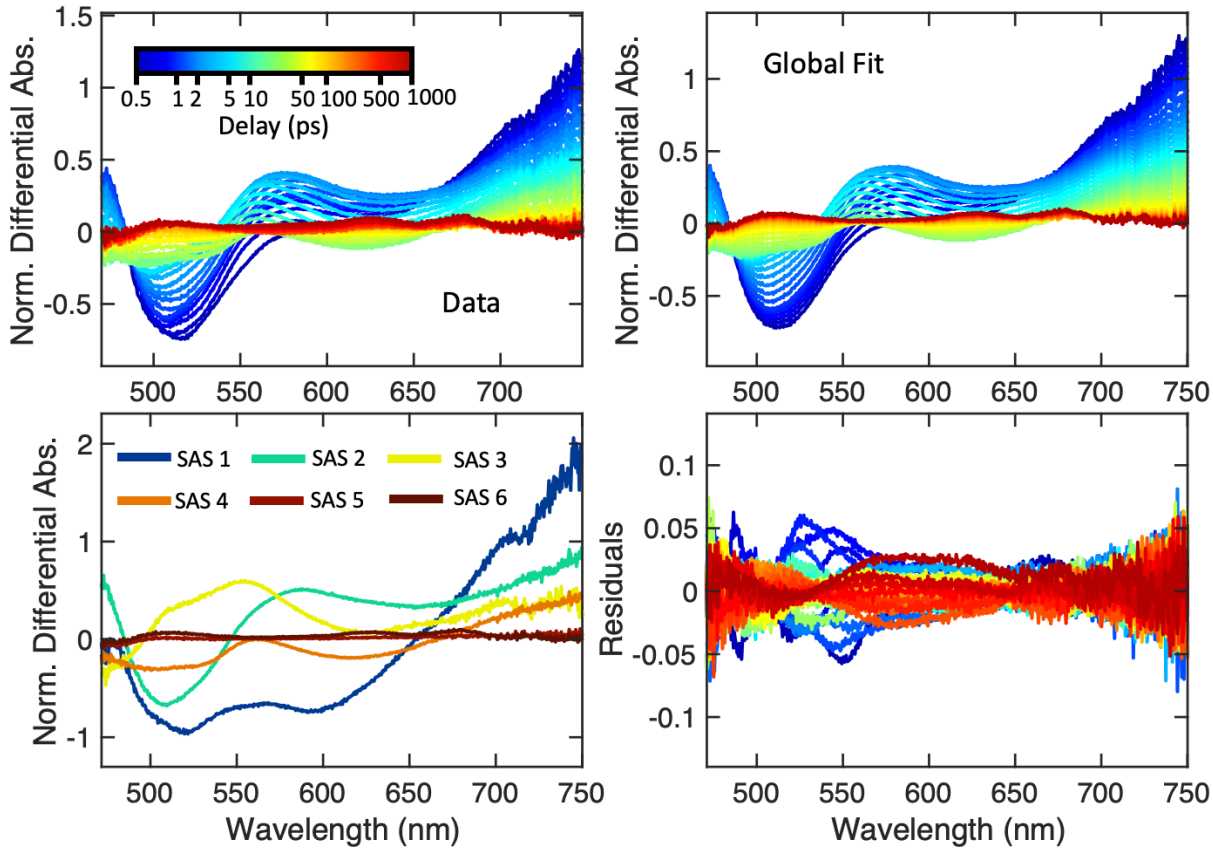


Figure S20. TAS of cis-4TCE excited at 475 nm: (top left) experimental data; (top right) global fit; (bottom left) species associated spectra; (bottom right) residuals. TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths

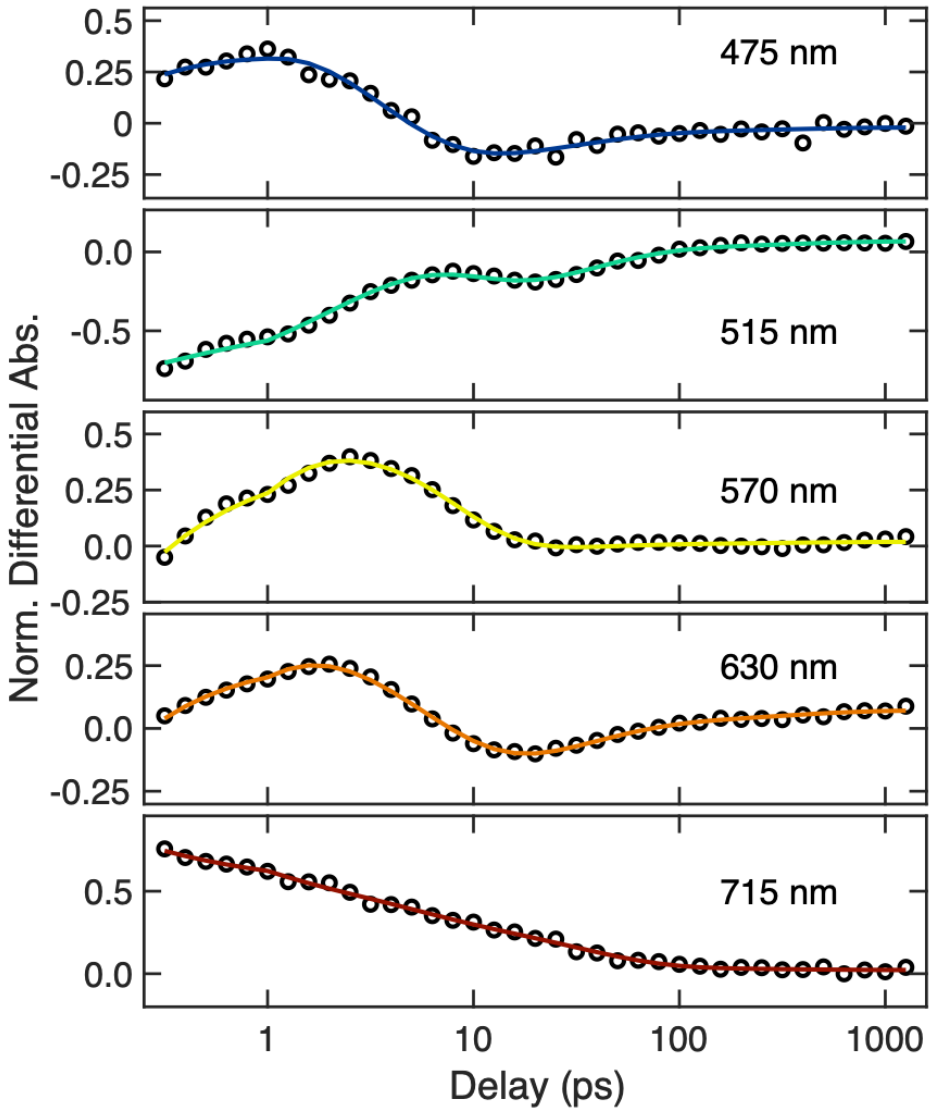


Figure S21. TAS of cis-4TCE excited at 475 nm: Time-dependent absorption at selected wavelengths (circles) with global fits (solid lines). TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths.

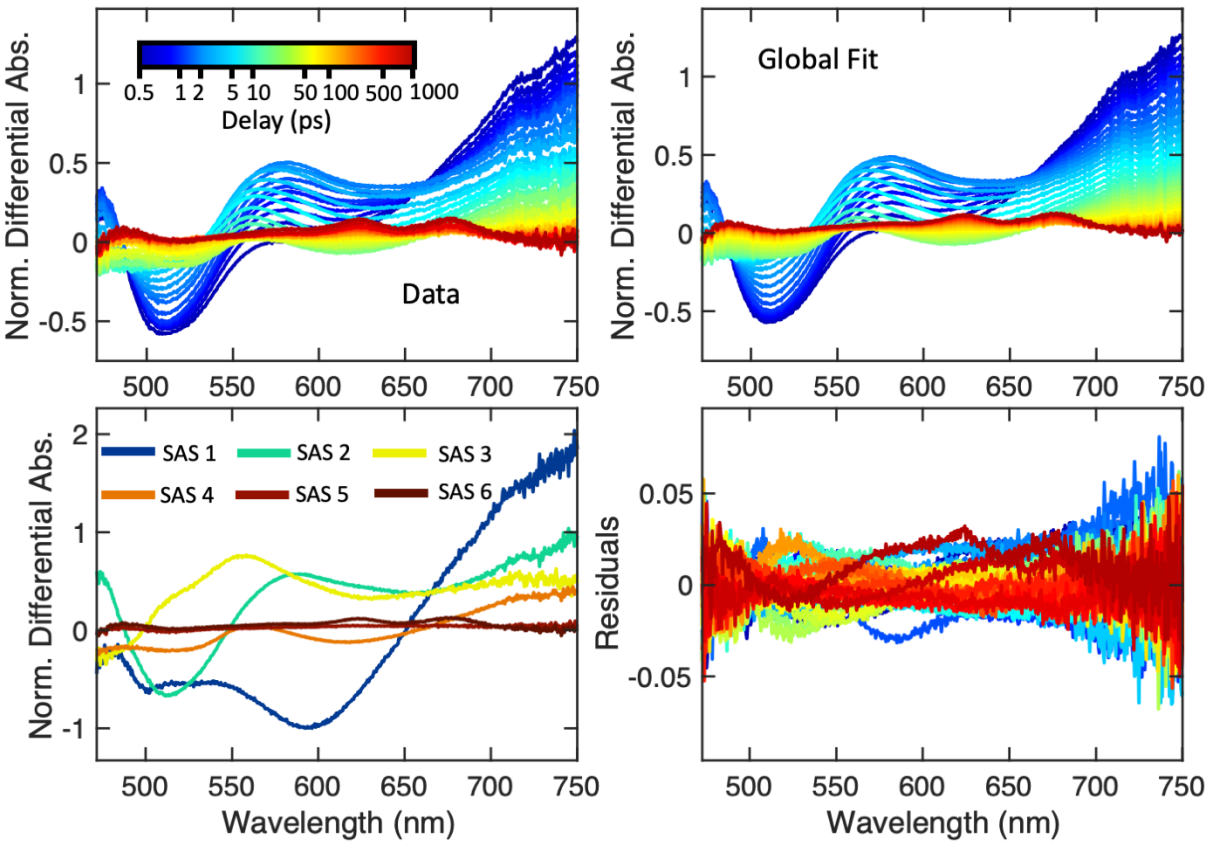


Figure S22. TAS of cis-4TCE excited at 470 nm: (top left) experimental data; (top right) global fit; (bottom left) species associated spectra; (bottom right) residuals. TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths

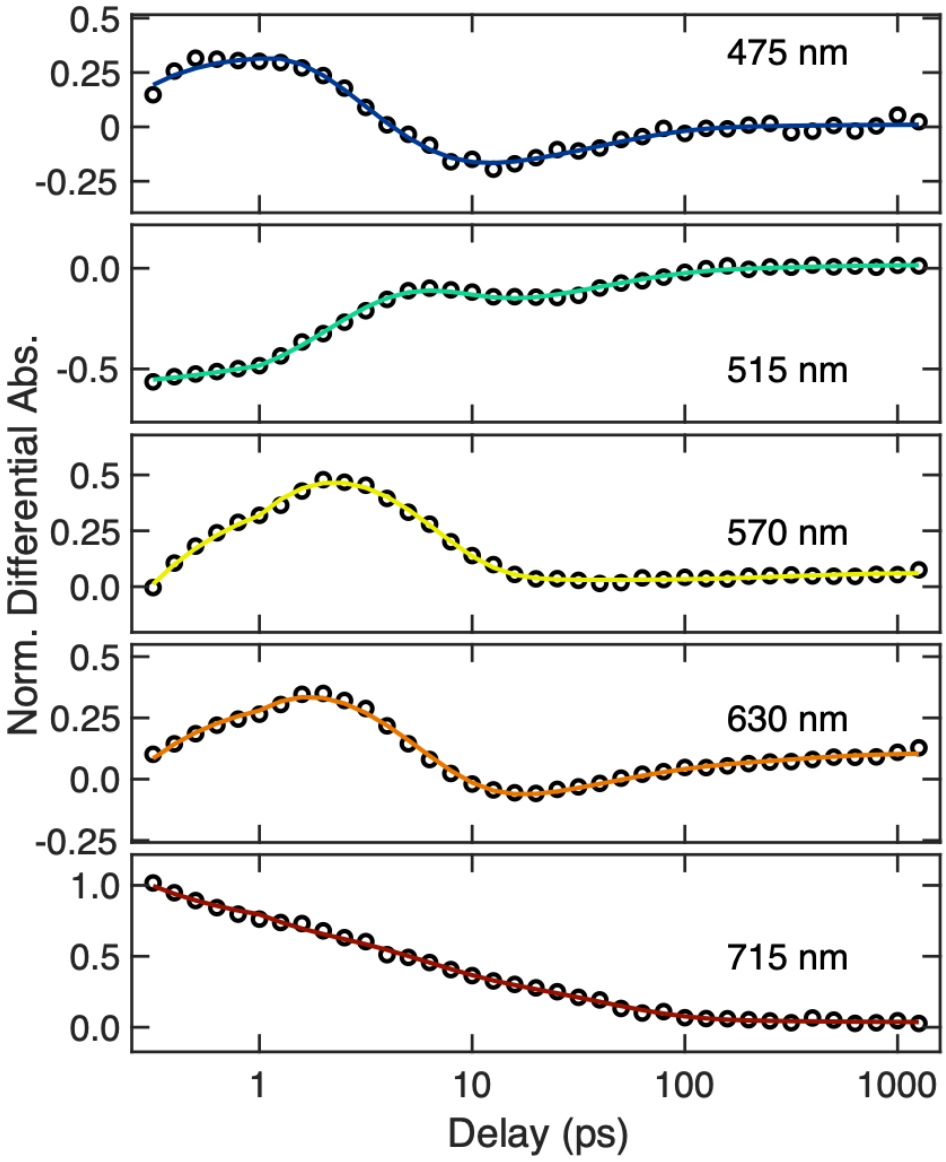


Figure S23. TAS of cis-4TCE excited at 470 nm: Time-dependent absorption at selected wavelengths (circles) with global fits (solid lines). TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths.

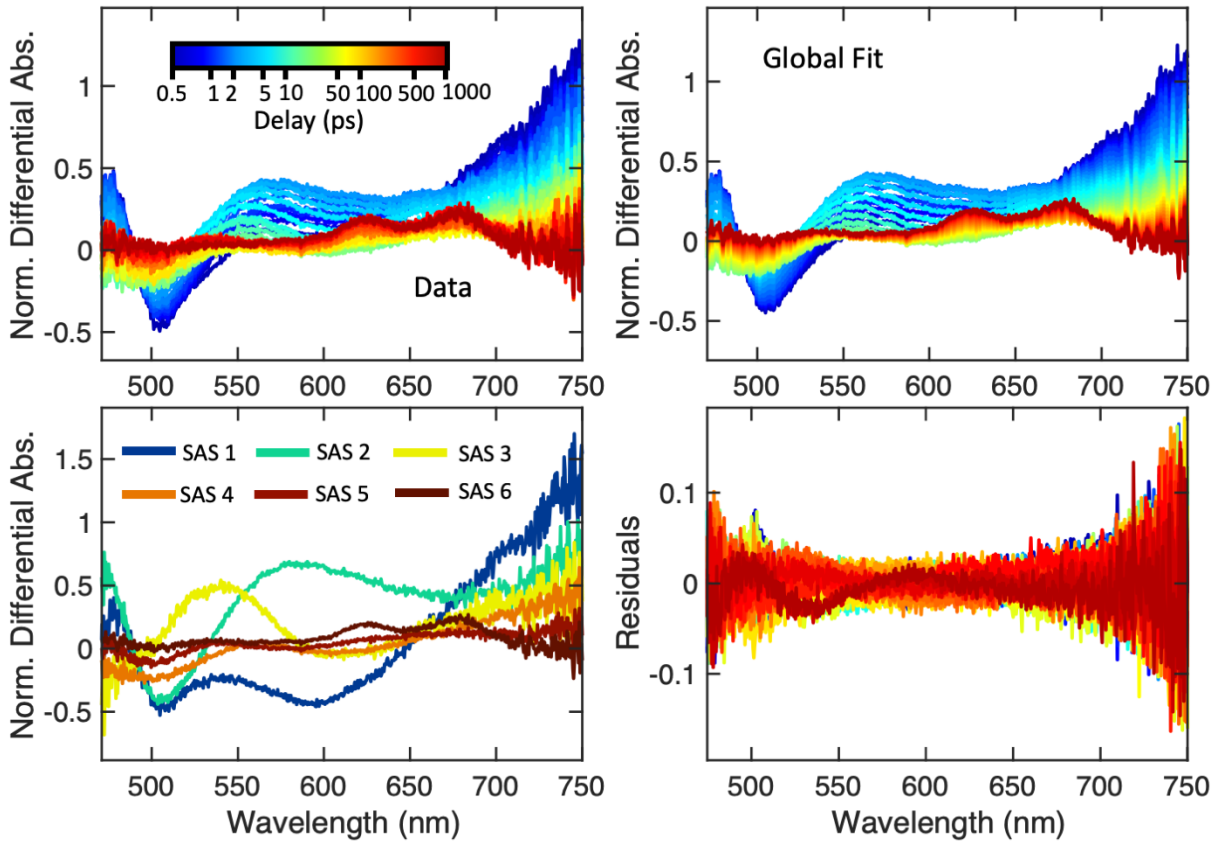


Figure S24. TAS of cis-4TCE excited at 460 nm: (top left) experimental data; (top right) global fit; (bottom left) species associated spectra; (bottom right) residuals. TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths

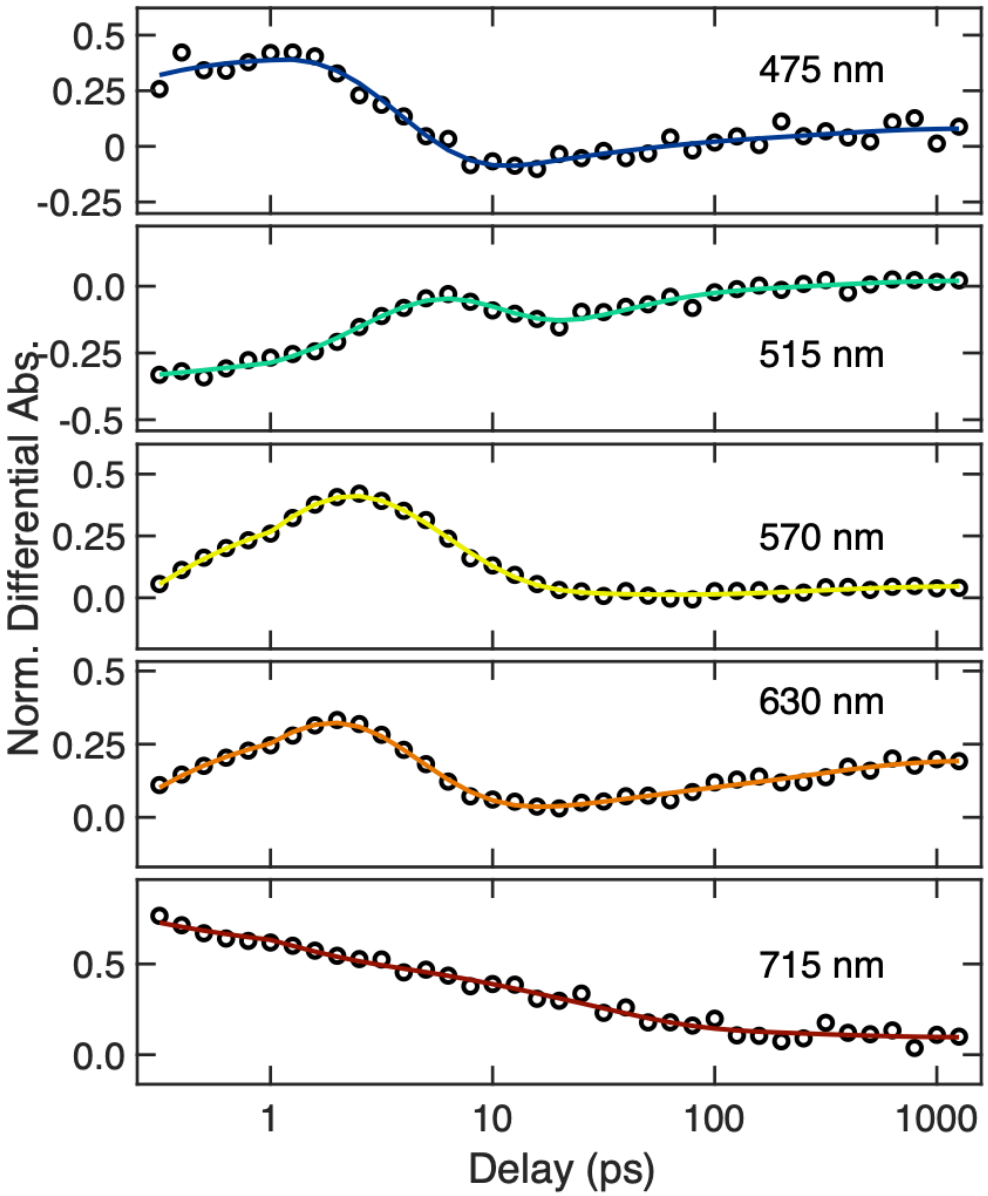


Figure S25. TAS of cis-4TCE excited at 460 nm: Time-dependent absorption at selected wavelengths (circles) with global fits (solid lines). TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths.

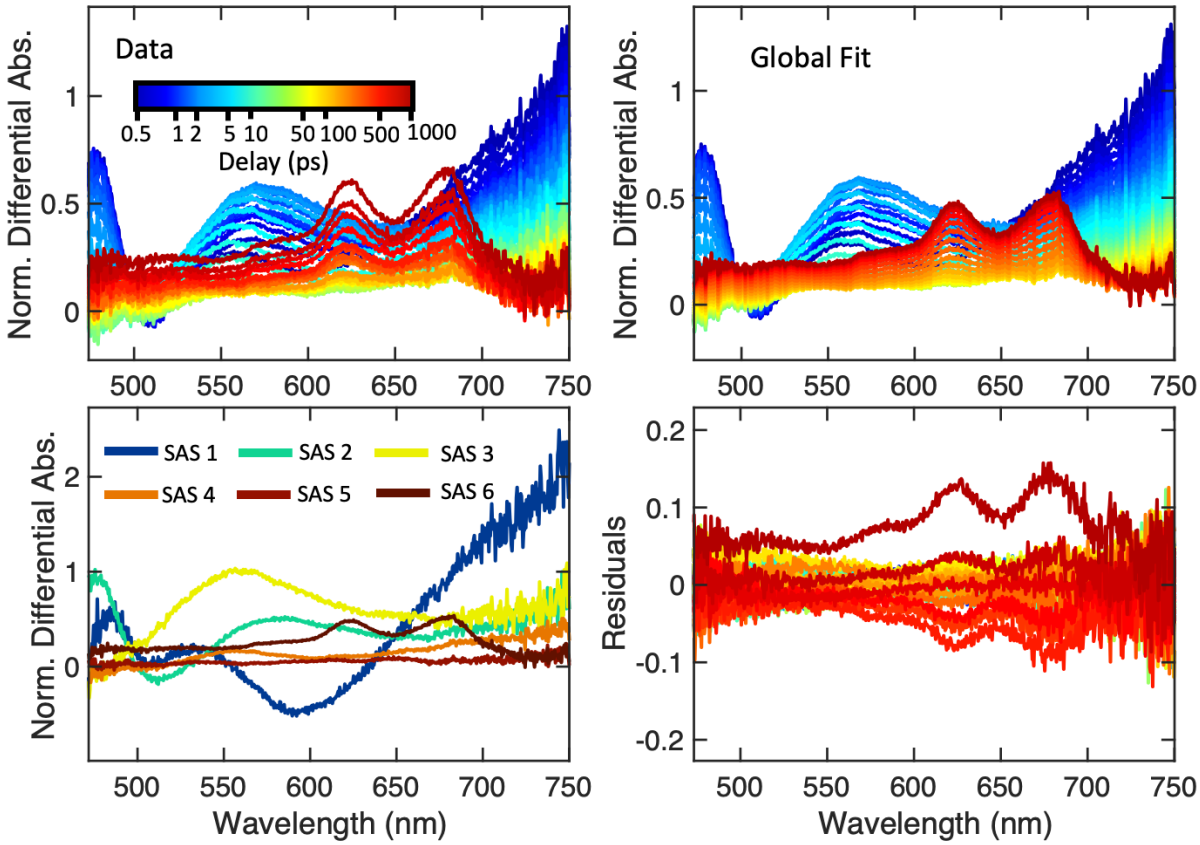


Figure S26. TAS of cis-4TCE excited at 440 nm: (top left) experimental data; (top right) global fit; (bottom left) species associated spectra; (bottom right) residuals. TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths

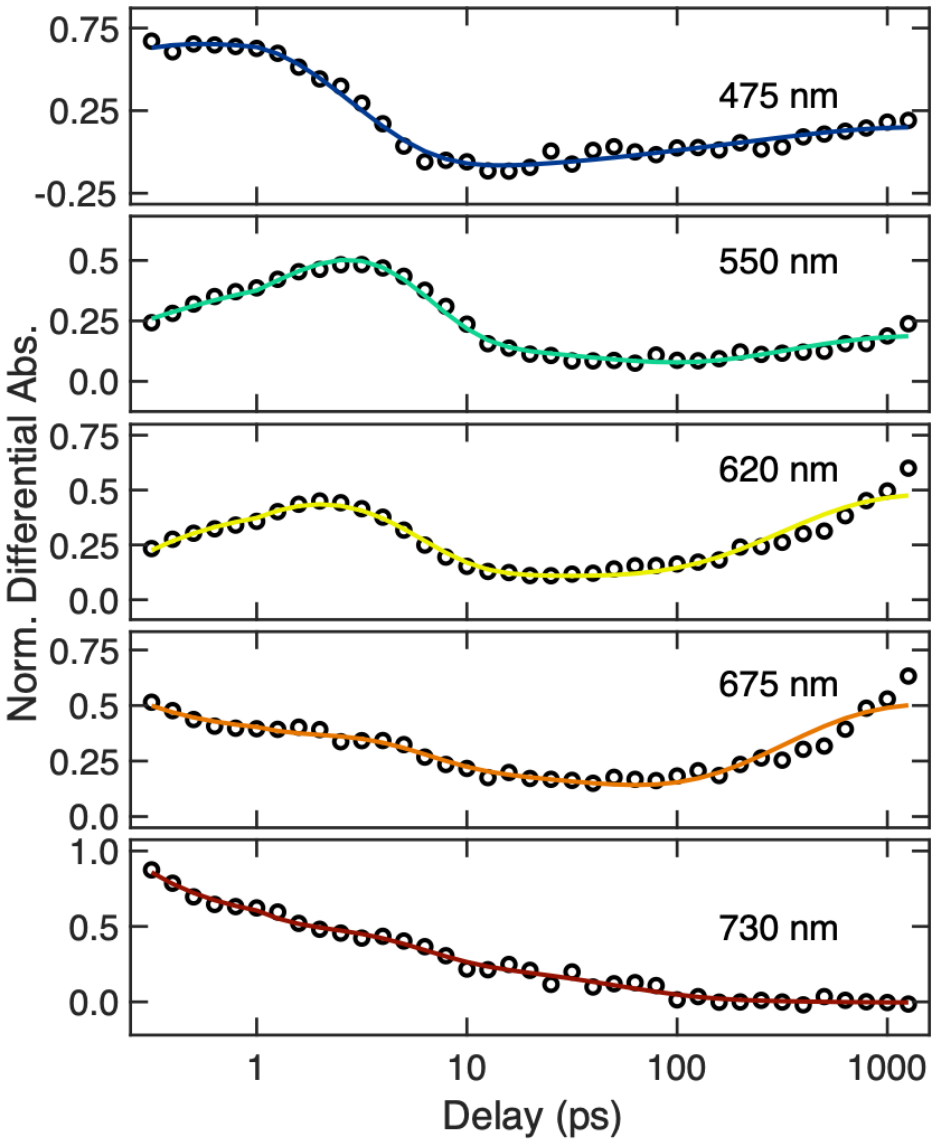


Figure S27. TAS of cis-4TCE excited at 440 nm: Time-dependent absorption at selected wavelengths (circles) with global fits (solid lines). TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths.

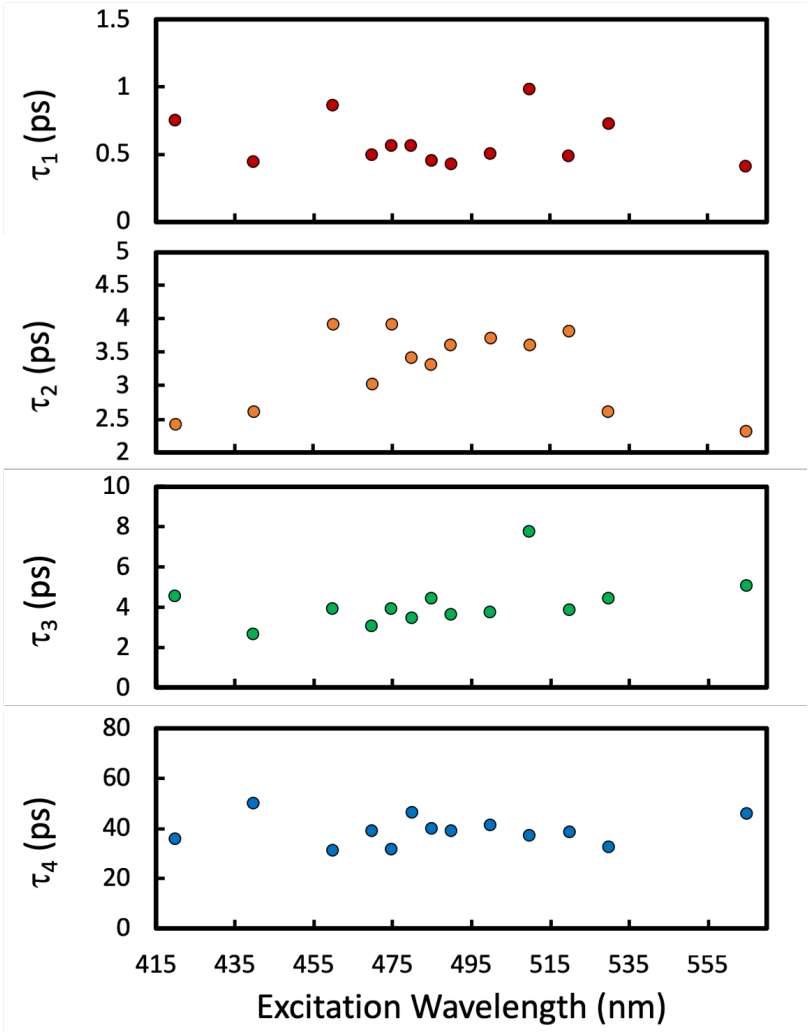


Figure S28. Plot of first four relaxation lifetimes with variation in excitation wavelength for cis-4TCE.

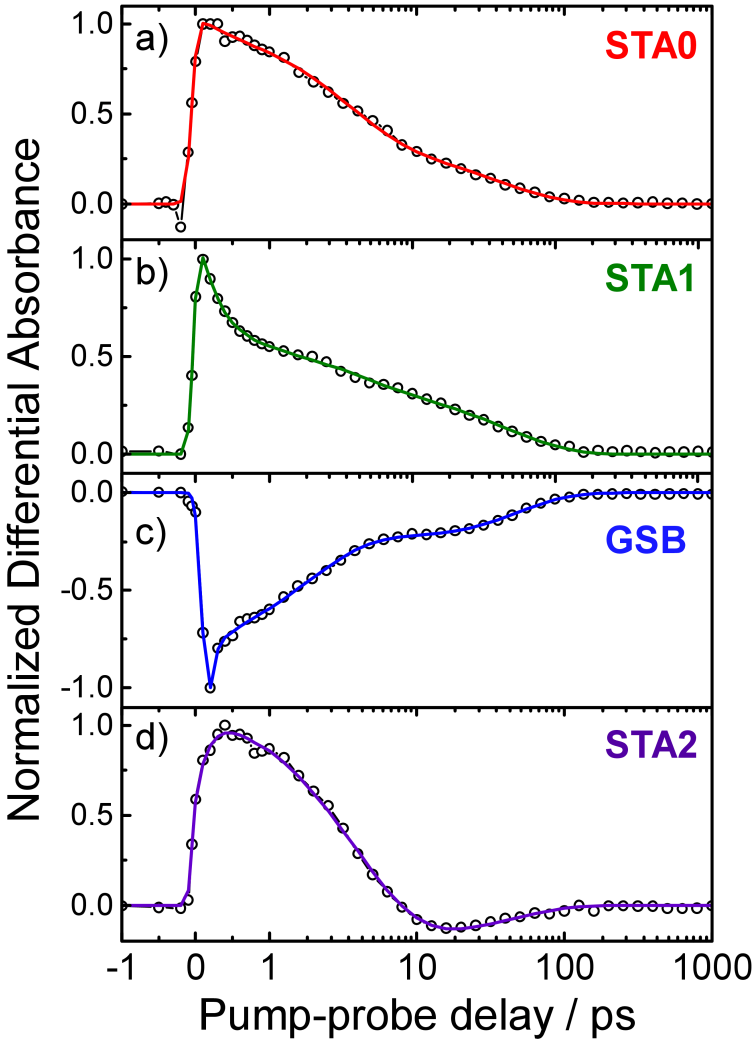


Figure S29. Cuts through TAS data collected with 530 nm excitation at wavelengths characteristic of features STA0 (1050 nm), STA1 (750 nm), GSB (520 nm) and STA2 (450 nm). Each trace is fit with a multiexponential convoluted with instrument response to characterize the fastest signal evolutions

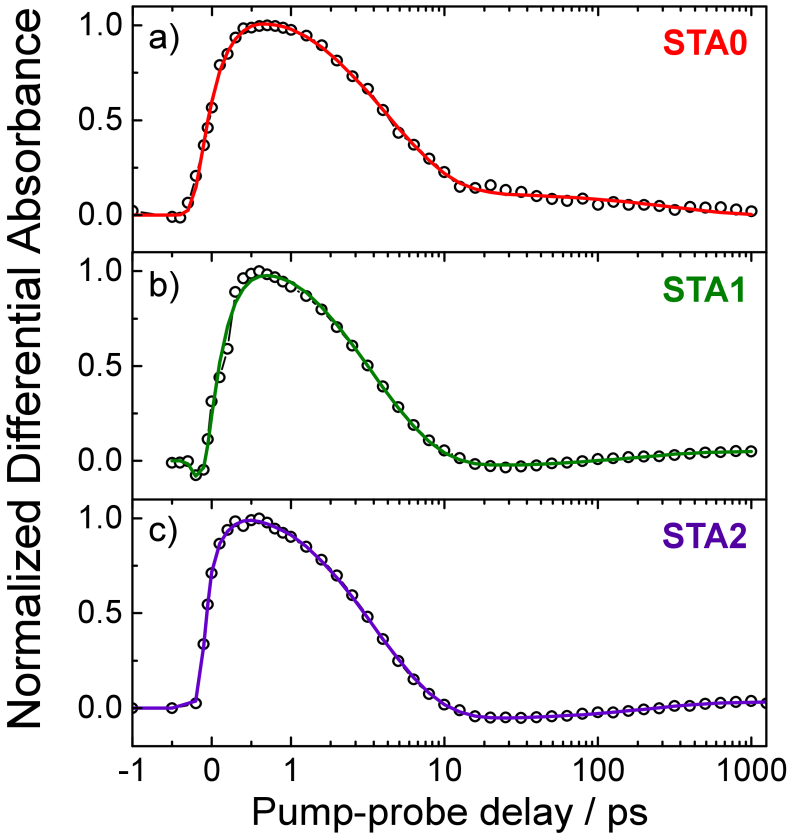


Figure S30. Cuts through TAS data collected with 530 nm excitation at wavelengths characteristic of features STA0 (1050 nm), STA1 (750 nm), and STA2 (450 nm). Each trace is fit with a multiexponential convoluted with instrument response to characterize the fastest signal evolutions

Table S1. Parameters for fitting single wavelength cuts through TAS data collected with 530 and 420 nm excitation of cis-4TCE. Each traces was fitted with a multiexponential function

$$I(t) = \sum_i A_i \exp\left(-t/\tau_i\right)$$

convoluted with the temporal instrument response. ("-" denotes a rising component.)

	530 nm Excitation				420 nm Excitation		
	STA0	**STA1**	**GSB**	**STA2**	**STA0**	**STA1**	**STA2**
A_1	-	0.65	-	(-)0.77	(-)1.29	(-)1.91	(-)0.66
τ_1 /ps	-	0.29	-	0.20	0.30	0.28	0.30
A_2	0.70	0.25	(-)0.61	1.42	1.18	1.41	1.35
τ_2 /ps	3.2	3.7	1.8	3.9	4.3	3.4	3.5
A_3	0.34	0.36	(-)0.43	(-)0.23	0.12	(-)0.08	(-)0.10
τ_3 /ps	35.8	46.1	39.9	39.7	303.1	179.8	219.4
A_4	-	-	0.21	-	-	-	-
τ_4 /ps	-	-	17.0	-	-	-	-
Offset	-	-	-	-	-	0.05	0.03

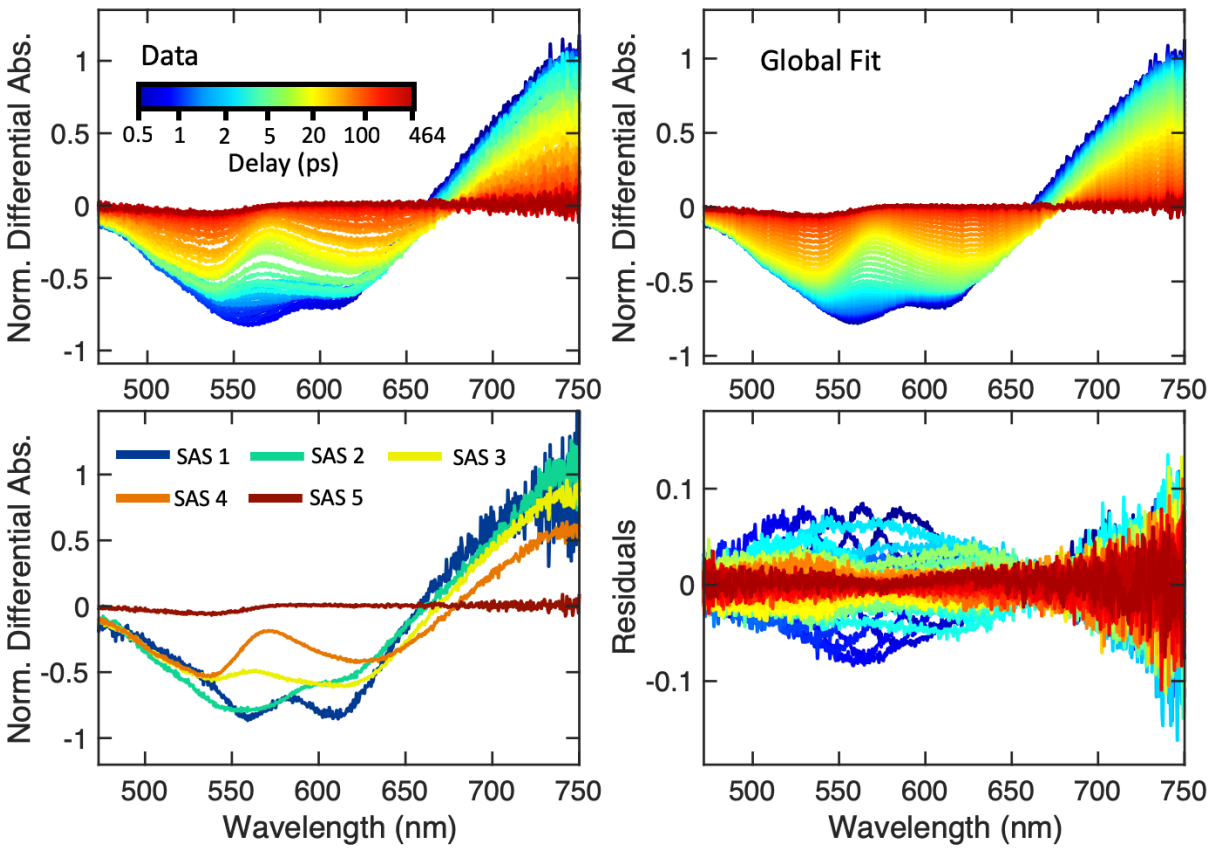


Figure S31. TAS of brominated trans-4TCE **(2)** excited at 530 nm: (top left) experimental data; (top right) global fit; (bottom left) species associated spectra; (bottom right) residuals. TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths

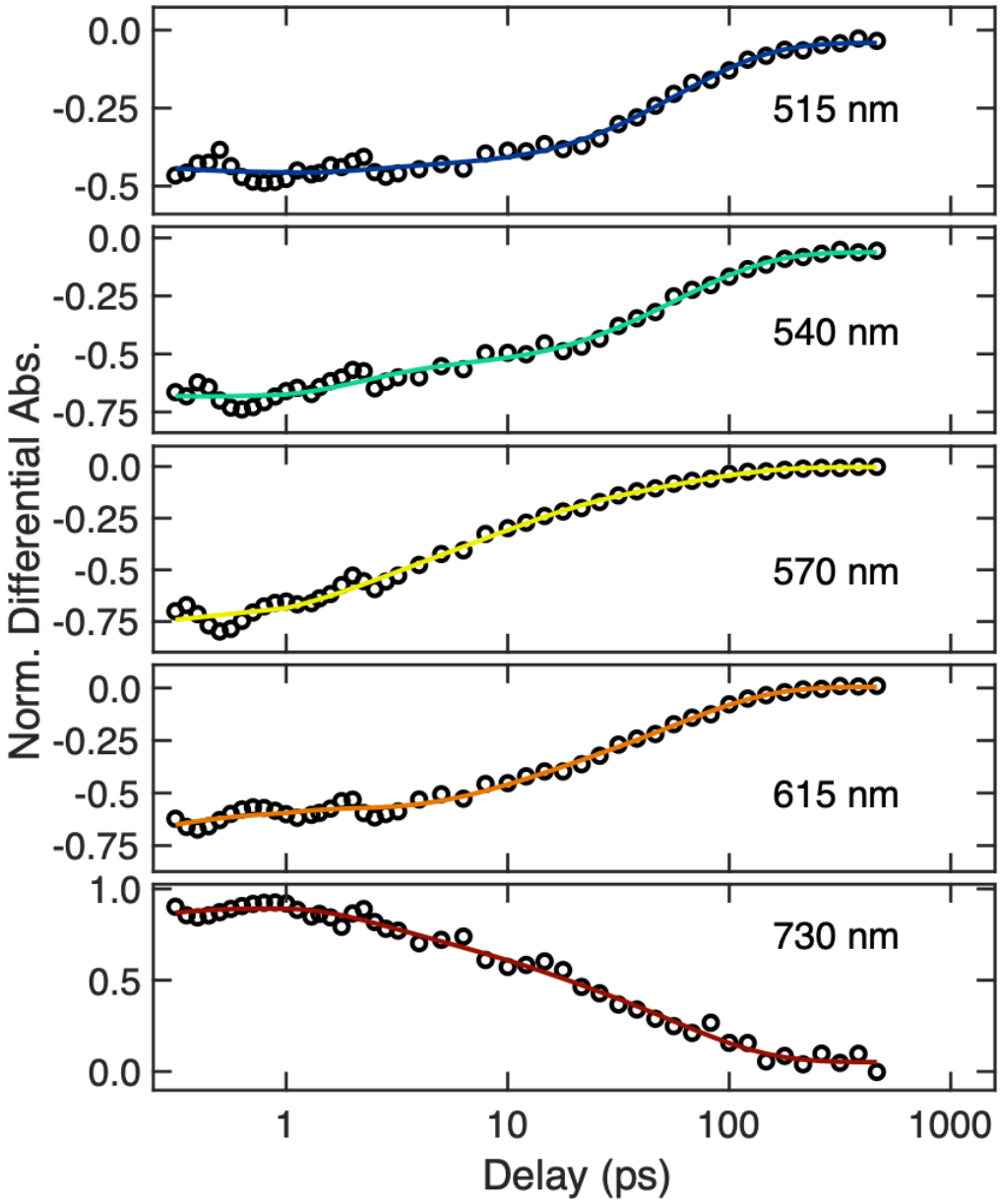


Figure S32. TAS of brominated trans-4TCE **(2)** excited at 530 nm: Time-dependent absorption at selected wavelengths (circles) with global fits (solid lines). TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths.

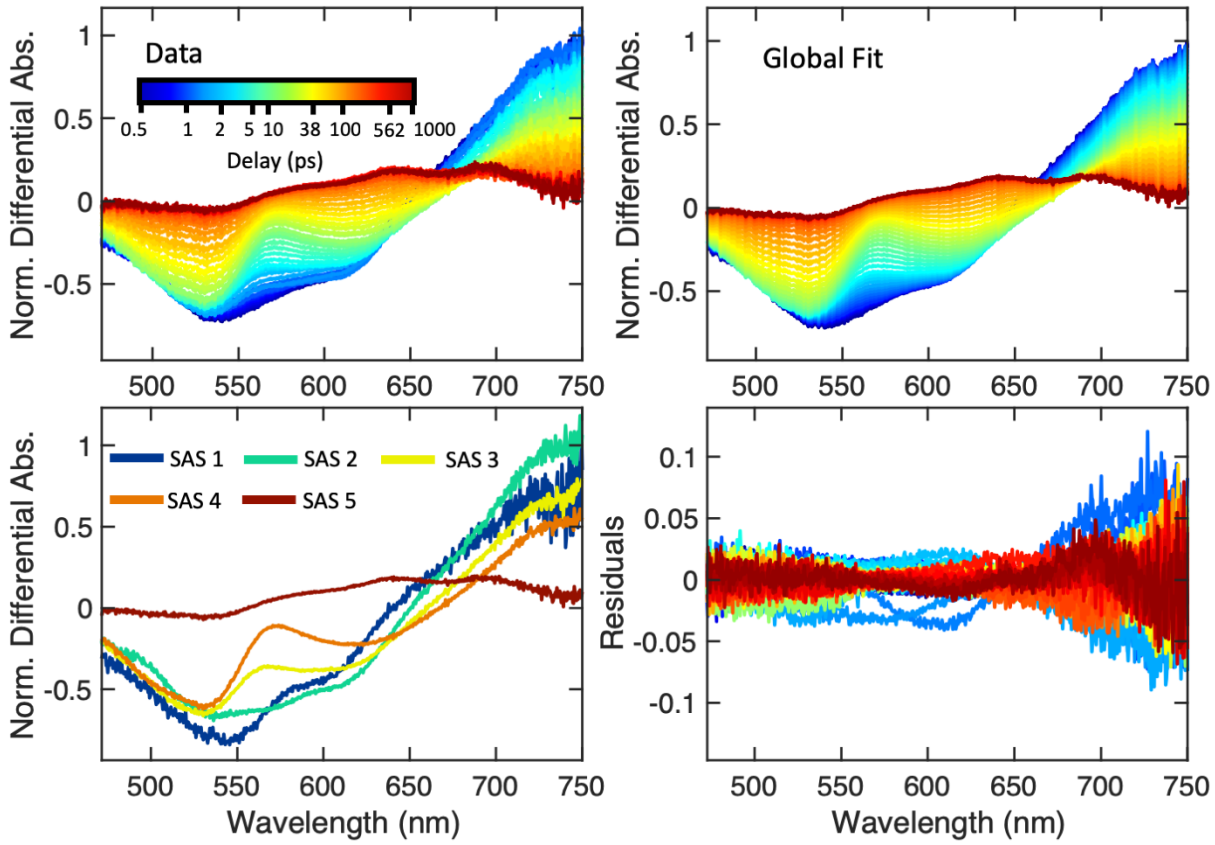


Figure S33. TAS of brominated trans-4TCE **(2)** excited at 420 nm: (top left) experimental data; (top right) global fit; (bottom left) species associated spectra; (bottom right) residuals. TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths

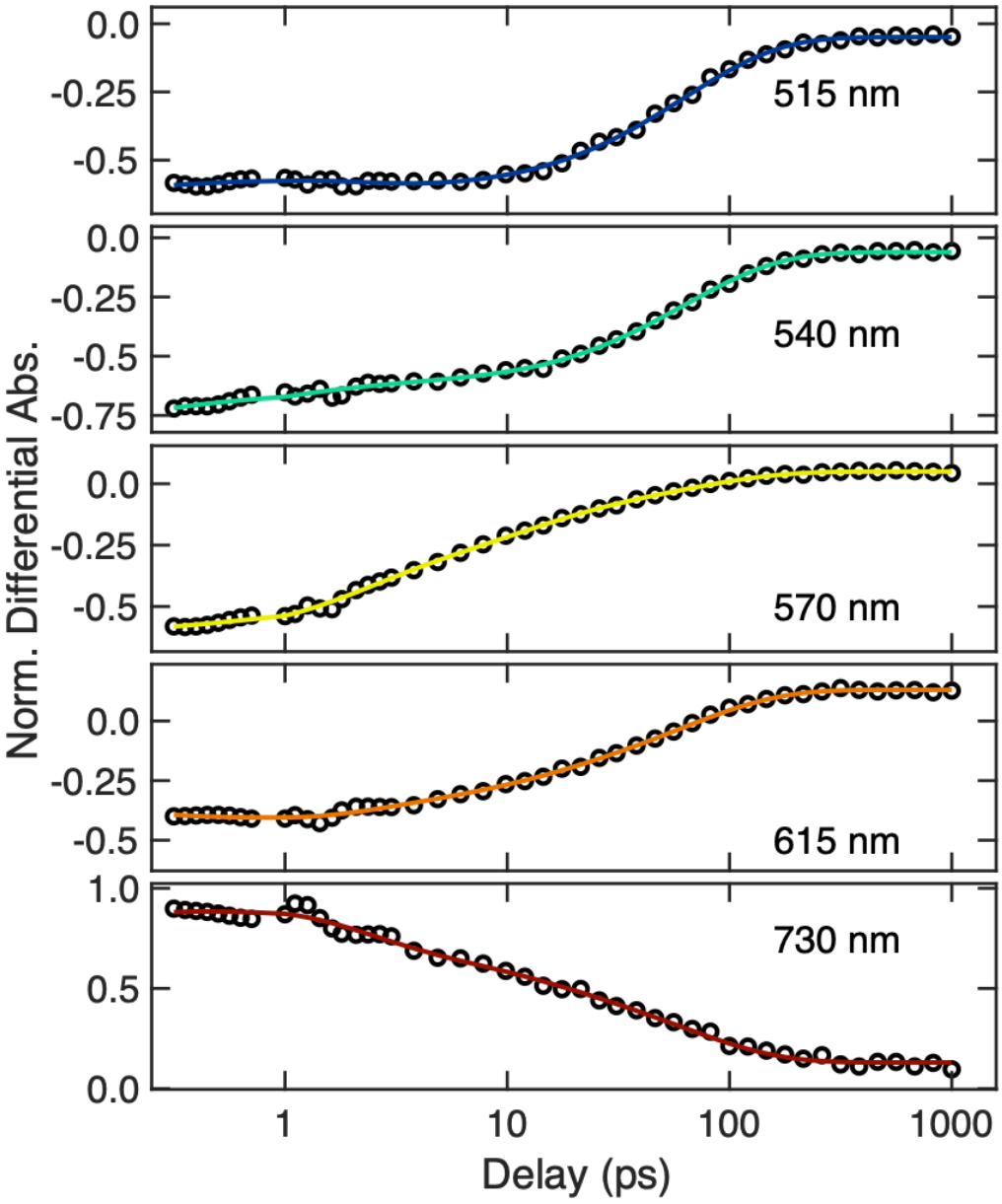


Figure S34. TAS of brominated trans-4TCE **(2)** excited at 420 nm: Time-dependent absorption at selected wavelengths (circles) with global fits (solid lines). TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths.

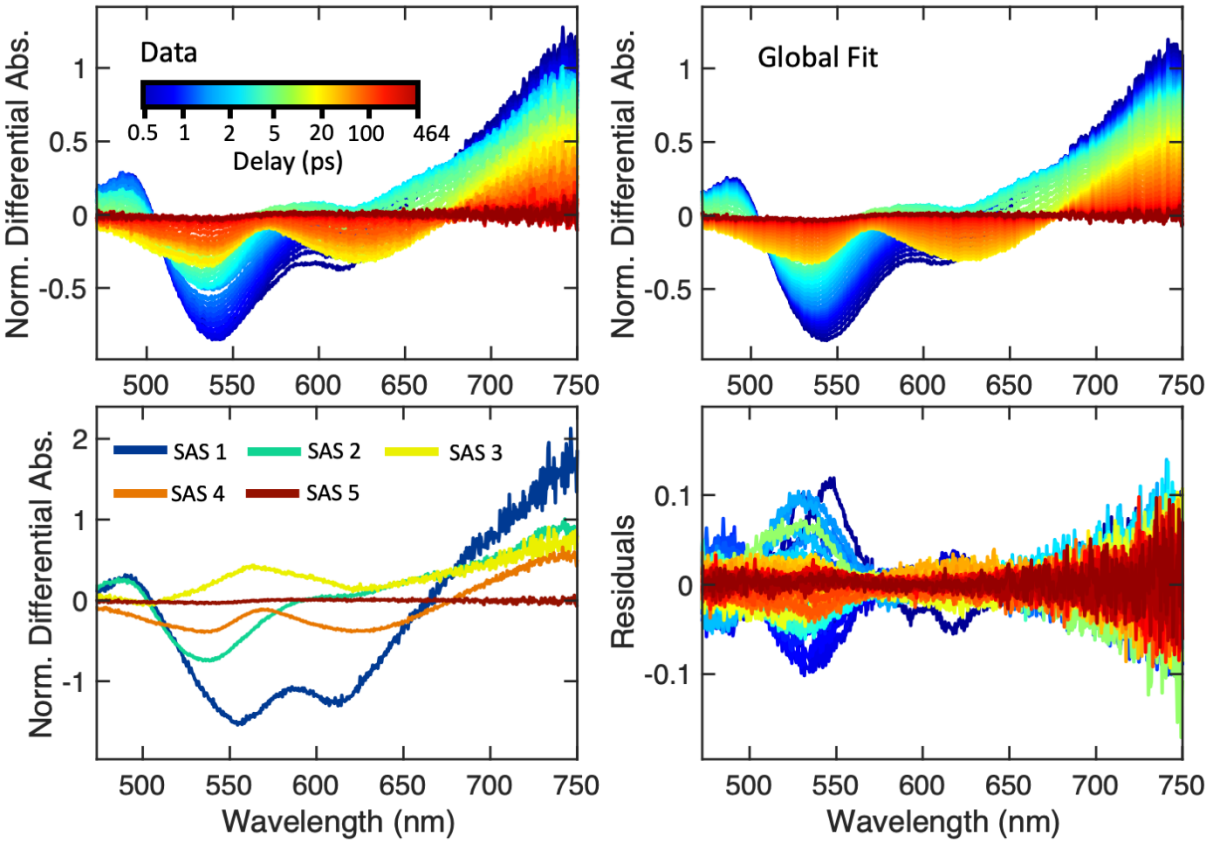


Figure S35. TAS of brominated cis-4TCE **(2)** excited at 530 nm: (top left) experimental data; (top right) global fit; (bottom left) species associated spectra; (bottom right) residuals. TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths

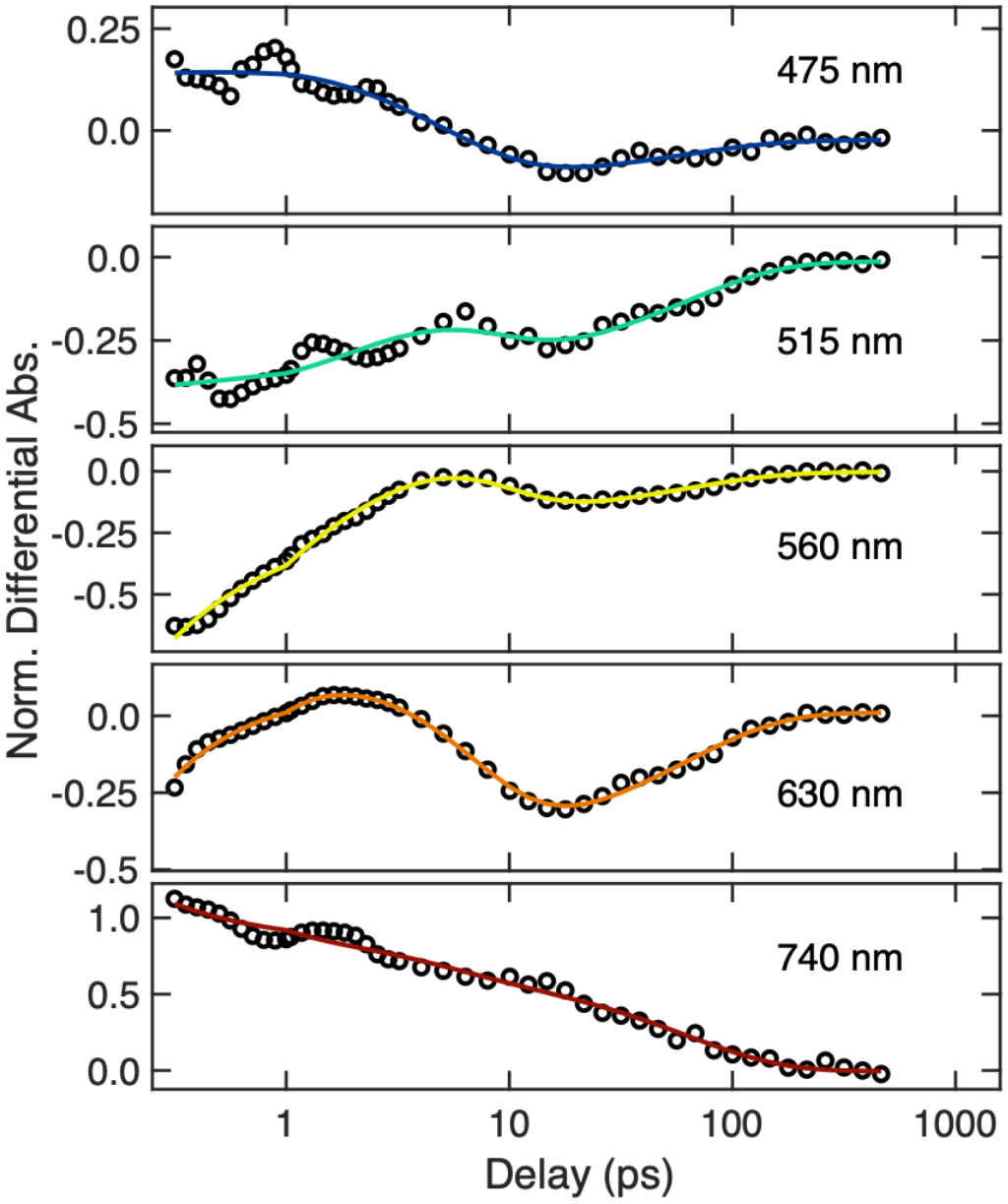


Figure S36. TAS of brominated cis-4TCE **(2)** excited at 530 nm: Time-dependent absorption at selected wavelengths (circles) with global fits (solid lines). TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths.

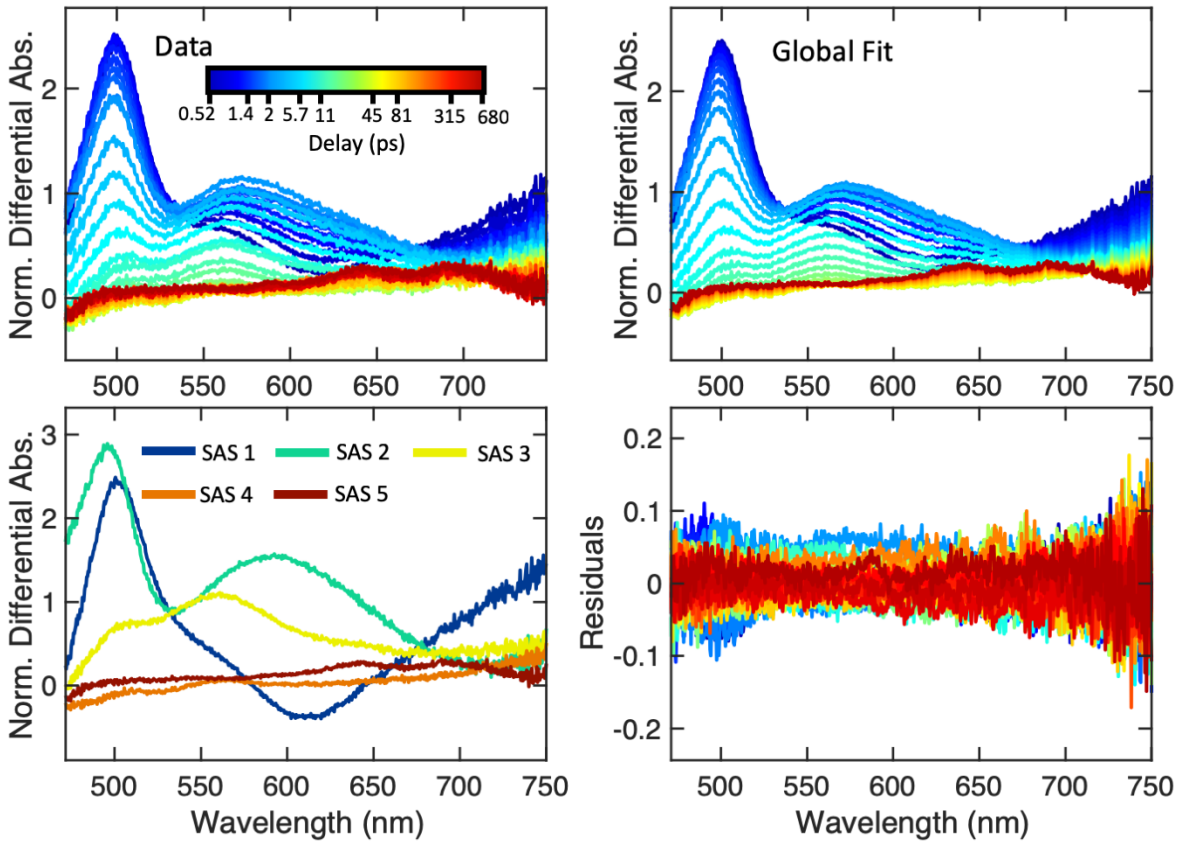


Figure S37. TAS of brominated cis-4TCE **(2)** excited at 420 nm: (top left) experimental data; (top right) global fit; (bottom left) species associated spectra; (bottom right) residuals. TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths

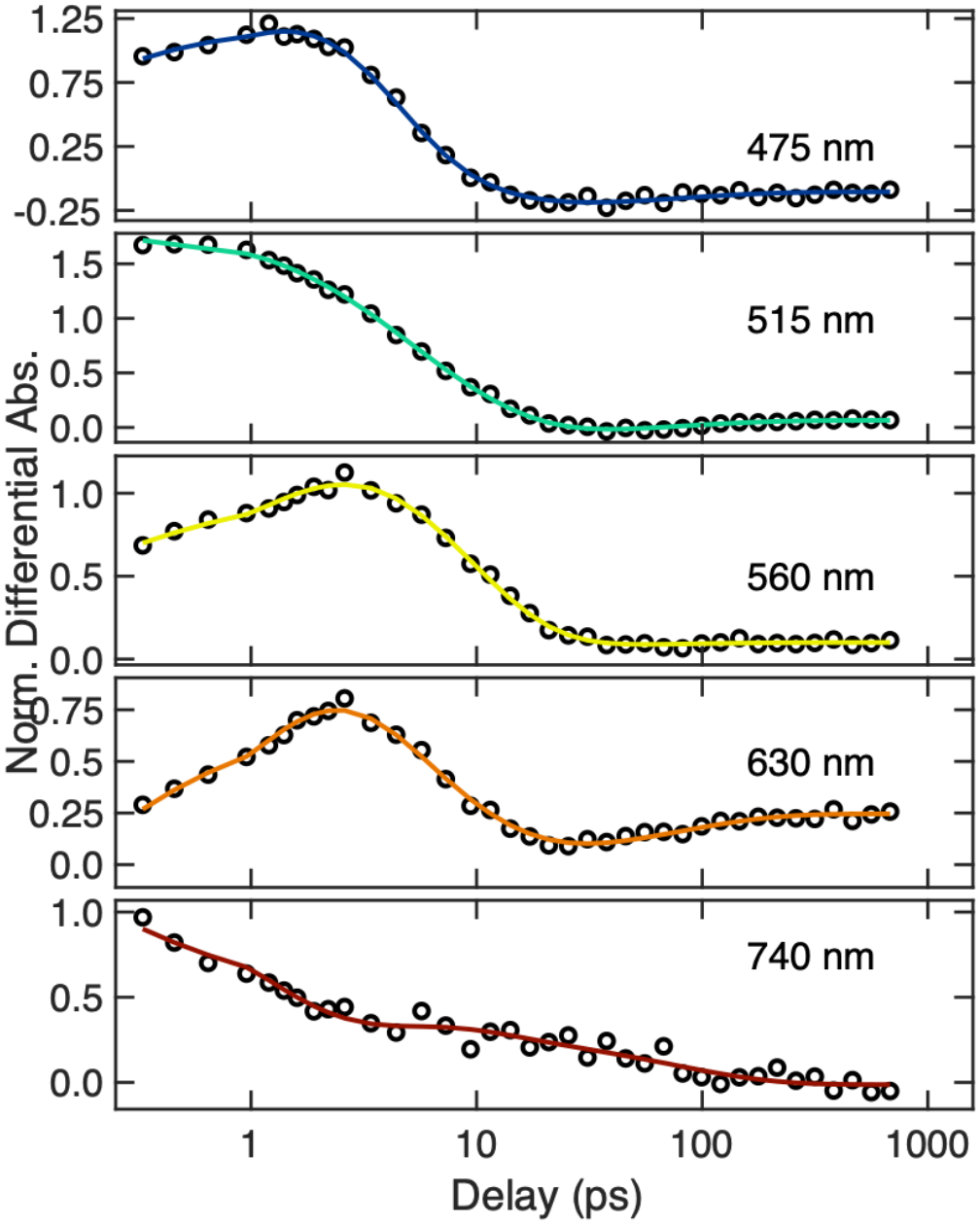


Figure S38. TAS of brominated cis-4TCE **(2)** excited at 420 nm: Time-dependent absorption at selected wavelengths (circles) with global fits (solid lines). TAS data has been normalized at 750 nm to enable comparisons across excitation wavelengths.

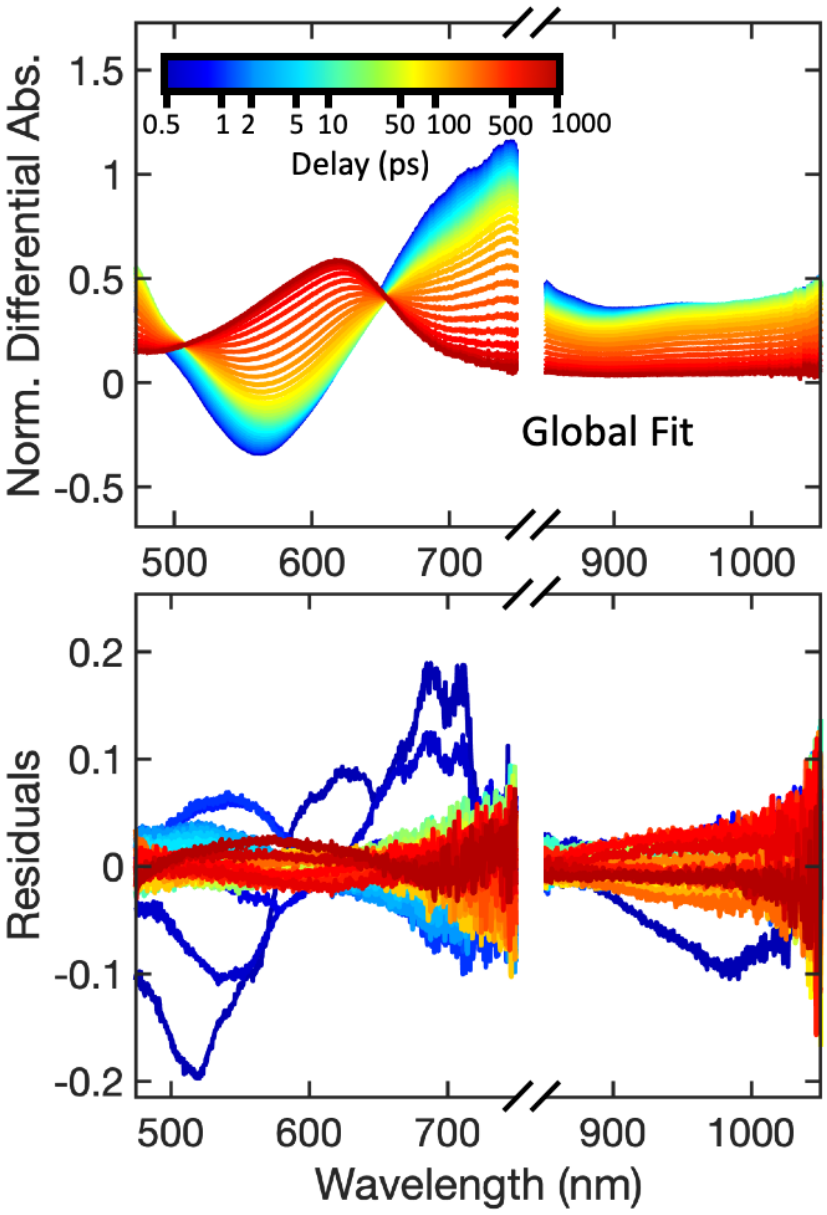
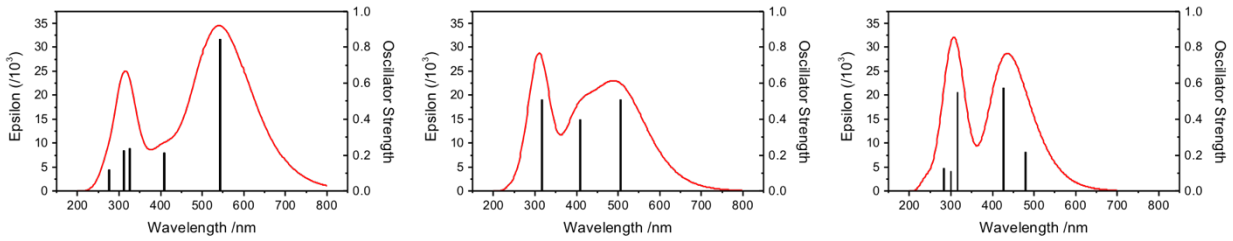


Figure S39. Global spectral fit (top) and residuals (bottom) for TAS data of **(3)** collected with 490-nm excitation.



AP Conformer	
Wavelength /nm	Oscillator Strength
541.62	0.8453
408.51	0.2161
325.02	0.2392
310.28	0.2278
274.75	0.1204

P_A Conformer	
Wavelength /nm	Oscillator Strength
505.68	0.5091
407.88	0.4004
316.05	0.5092

P_B Conformer	
Wavelength /nm	Oscillator Strength
478.04	0.2199
426.01	0.5749
314.96	0.55120
299.05	0.1121
282.30	0.1270

Figure S40. Calculated absorption spectrum and table of vertical excitation energies and oscillator strengths for three cis-4TCE conformers.

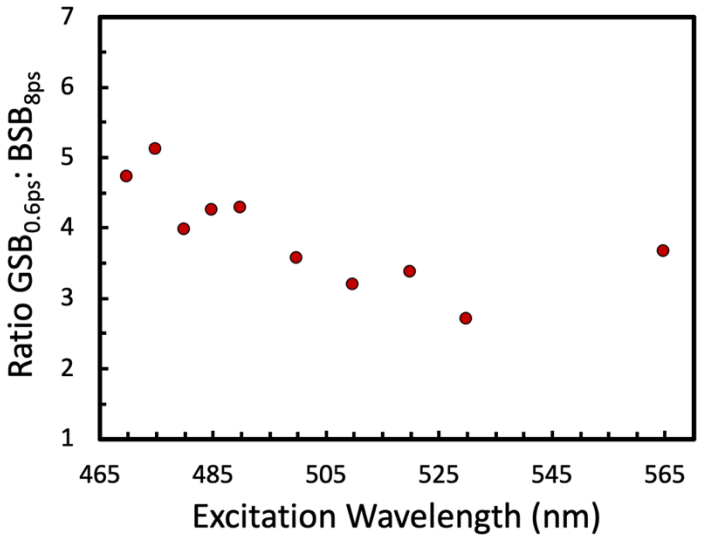


Figure S41. Ratio of GSB at 0.6ps to GSB at 8ps. GSB intensity was averaged between 500 and 530nm. The average ratio across all wavelengths is 3.9 ± 0.7.

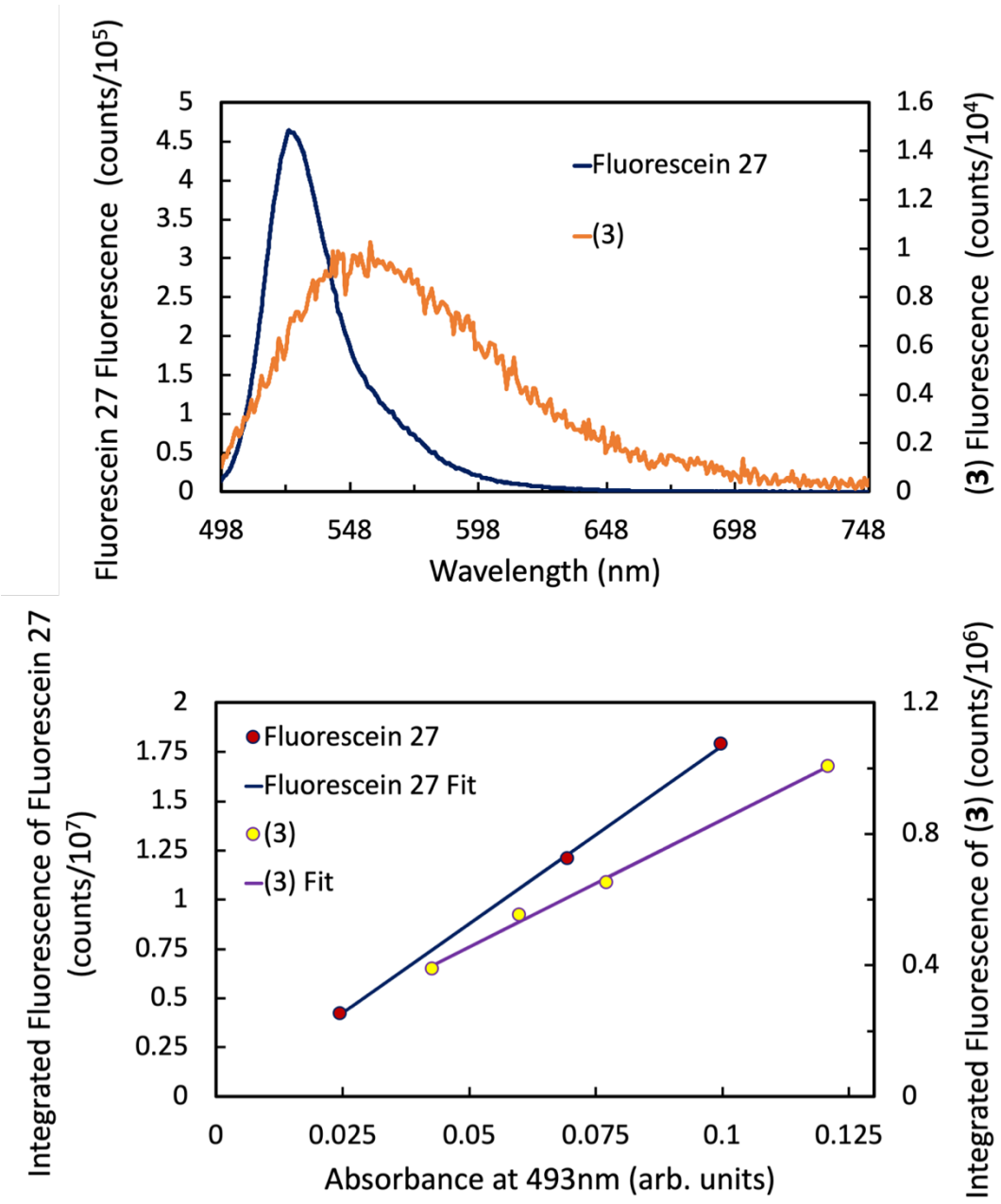


Figure S42. Fluorescence of Fluorescein 27 and **(3)** (Top), and linear fits from a fluorescence quantum yield experiment using Fluorescein 27 in 0.1M KOH as a fluorescence standard.[1]

[1] Grabolle, M.; Spieles, M.; Lesnyak, V.; Gaponik, N.; Eychmuller, A.; Resch-Genger, U., *Anal, Chem.* **2009**, 81, 6285-6294.