Supporting Information for
"Ultrafast Dynamics in DNA: 'Fraying' at the End of the Helix"

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The choice of α leads to modest spectral shifts throughout the time range of the transient absorption spectrum. Figure S1 shows the effect of changing α on the earliest measured spectrum. The range of α can be limited by the requirement that the earliest measured spectrum should not be narrower than the glass spectrum nor should it have a higher mean frequency than the glass spectrum. Both values of α shown in Figure S1 satisfy this requirement.

A more stringent, but less rigorous, criterion for judging the value of α is that the TRSS results should extrapolate smoothly to the glass spectrum at zero time. In other words, the glass spectrum should be a good estimate of the spectrum before diffusive motion begins. This criterion is better satisfied for larger values of α, i.e., $\alpha \sim 1$.

A simple power-law fit to the data has a physically incorrect divergence at $t = 0$. The parameter t_0 in eqs 3 and 5 is introduced to remove this divergence. However, this parameter does not strongly affect the fit to the data. As shown in Figure S2, t_0 primarily determines the behavior of the fit below the time range of the data. It does change the extrapolated value of the Stokes shift at zero time: t_0 = 15 fs gives $S(0)$ = -200 cm^{-1}, t_0 = 25 fs gives $S(0)$ = 0 cm^{-1} and t_0 = 50 fs gives $S(0)$ = +200 cm^{-1} (Figure S2). The expectation that the spectrum in the glass is a good estimate of the early time spectrum, i.e., that $S(0)$ = 0 cm^{-1}, leads to the final choice of t_0, 25 fs in this data set. Although this value leads to a simple self-consistent picture of the spectroscopy, the value of t_0 has little affect on the overall quality of the fits to the data or the values of α or S_∞.

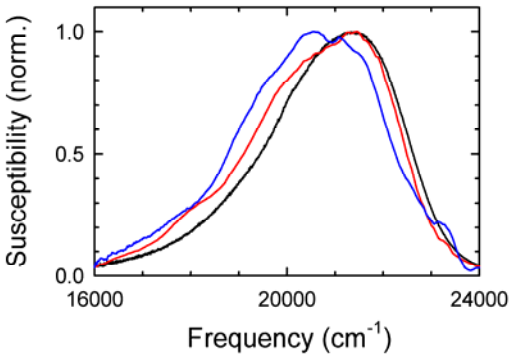

Figure S1. The emission spectrum at 40 fs derived from the transient absorption spectrum using different values of α: α = 0 (blue) and α =1 (red), compared to the steady-state emission spectrum in a glass (black). The data are from the centered sequence.

In the simplest case, the excited-state absorption spectrum of coumarin extracted from the transient absorption measurements would be the same when the coumarin is in either the centered or helix-end sequences. Figure S3 compares these two spectra. They do have the same width and basic shape, but the helix-end spectrum is shifted 900 cm^{-1} to higher frequency. The absorption spectrum for the helix-end sequence is also shifted to higher frequency, but by only 200 cm^{-1}. Little is known about the effects of environment on higher lying electronic states in coumarin, so it is impossible to say if this result is reasonable or not. However, it again illustrates that these effects need to be considered when analyzing transient absorption measurements.

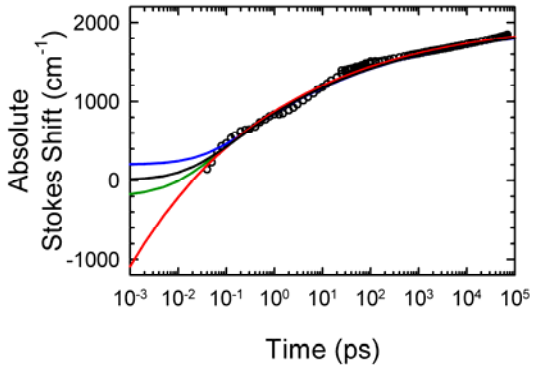

Figure S2. The effect of t_0 on the fit to the data is to change the extrapolated Stokes shift at zero time: t_0 = 50 (green), t_0 = 25 (black), (this value is used in paper and shown in Fig. 8), t_0 = 15 fs (blue), t_0 = 0 fs (red, a simple power-law without a short-time cut off). The data are the same as in Figure 8 of the paper.

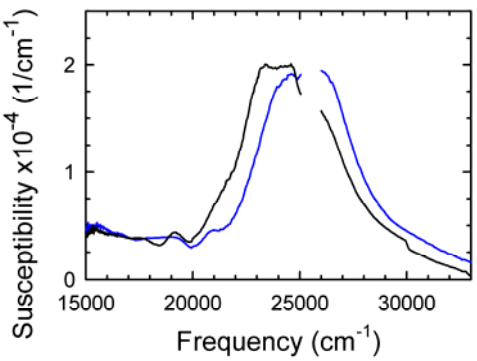

Figure S3. Excited-state absorption spectra of the centered (black) and helix-end (blue) sequences at 65 ps derived from transient-absorption data.

Table S1. Parameters for the fits to eq 3 and 5 in Figures 8 and 9.

	α =1		α = 0.5	
	centered	helix-end	centered	helix-end
S_∞ (cm^{-1})	2063	2333	2101	2200
n	0.16	0.16	0.14	0.14
t_0 (fs)	25	16	14	11
A	1	0.77	1	0.87
B	0	0.23	0	0.13
τ (ps)	–	5	–	5