Supporting Information for
"Power-Law Solvation Dynamics in DNA over Six Decades in Time"

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Data Collection and Analysis

Time-correlated single-photon (TCSPC) data were analyzed as previously described.[1] As is typically done, the steady-state emission spectrum was used to normalize the relative intensities of the different wavelength decays. Special care was taken to correct for scattered excitation light, which can distort the blue side of the emission spectrum.

Fluorescence up-conversion was done in a conventional manner using an unamplified Ti:sapphire laser.[2] The cross-correlation of excitation scattering and the gate pulse was less than 0.5 ps and results are only quoted at times greater than 1 ps. No attempt was made to deconvolve the instrument response. The different wavelength decays were normalized by matching the upconversion and TCSPC spectra at 65 ps. In other respects, the upconversion data was analyzed in the same manner as the TCSPC data. Both sets of spontaneous emission spectra were corrected to a susceptibility scale before calculating the first moment.[1] This procedure allows comparison of spontaneous-emission spectra with stimulated-emission spectra (below). Under simple assumptions, the absorption and emission spectra are mirror images on a susceptibility vs frequency scale. This condition holds quite closely for coumarin in DNA (Fig. S2)

Transient absorption data were collected over different time ranges with different step sizes (3 fs×0.7 ps, 10 fs×4.5 ps, 50 fs×32 ps and 200 fs×124 ps) with typically three repetitions of each scan. Corrections were made for the wavelength dependence of zero time, and Raman scattering from the solvent was subtracted.[3] Spectra from the total data set were binned in time and averaged using a bin width that is uniform on a logarithmic time scale.

A transient-absorption spectrum $\chi_{TA}(\omega, t)$ has three components: stimulated emission $\chi_{Em}(\omega, t)$, ground-state bleaching $\chi_{GS}(\omega, t)$ and excited-state absorption $\chi_{EA}(\omega, t)$. The ground-state bleach is approximated by the steady-state absorption spectrum $\chi_{Abs}(\omega)$ (Fig. S2) and assumed to be time-independent

$$\chi_{TA}(\omega,t)=\frac{1}{2-\kappa}\left(\chi_{Em}(\omega,t)+\chi_{Abs}(\omega)-\kappa\chi_{ES}(\omega,t)\right). \qquad (S1)$$

All the spectra are normalized to unit area on a susceptibility scale.[1,4] This normalization removes any effects of population decay. On a susceptibility scale, the absorption and stimulated emission spectra have equal amplitudes. However, the excited-state absorption spectrum and its relative amplitude κ are not independently known.

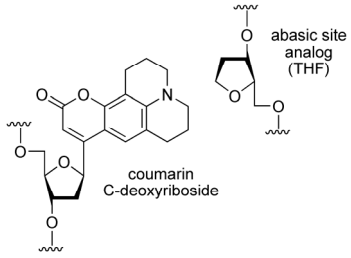

Figure S1. Structure of the coumarin riboside and corresponding abasic site. This pair mimics a regular base pair with minimal distortion to the DNA structure.

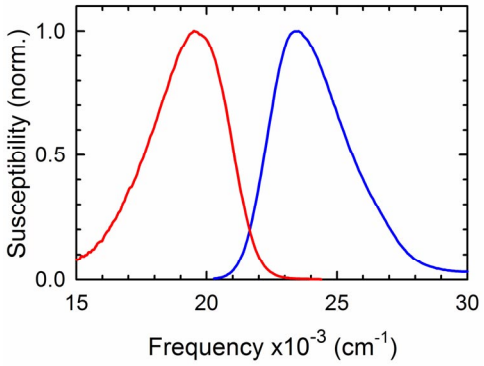

Figure S2. Excitation (blue) and emission (red) spectra in susceptibility units. The spectra have been normalized to unit amplitude. The excitation and emission spectra are almost mirror images of one another.

Examples of the transient absorption spectra are shown in Fig. S3. The shift of the stimulated emission component is evident even in these raw spectra.

However, to quantify the shift, the stimulated emission component must be isolated from the other components. Using the known absorption spectrum and the emission spectrum from TCSPC at 65 ps, the value of κ was determined, leading to the excited-state absorption spectrum at 65 ps $\chi_{EA}(\omega, 65\text{ ps})$. As is typical in the analysis of transient-absorption spectra, the determination of κ has an element of subjectivity. We employed three criteria: (1) The shape of the excited-state absorption spectrum should be 'reasonable'. The spectrum must be positive everywhere and should not show peaks or valleys corresponding to the bleach or emission spectra. (2) The earliest emission spectra should be close to the spectra in the glass. In particular,

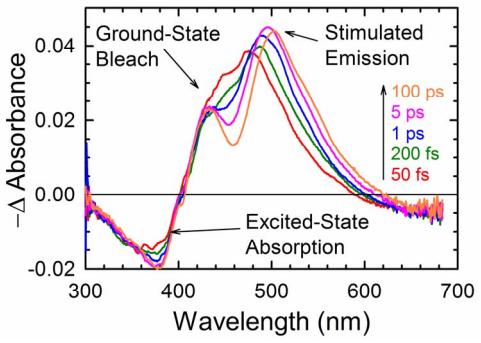

Figure S3. Transient absorption spectra at various times. Regions dominated by each of the three components are labeled.

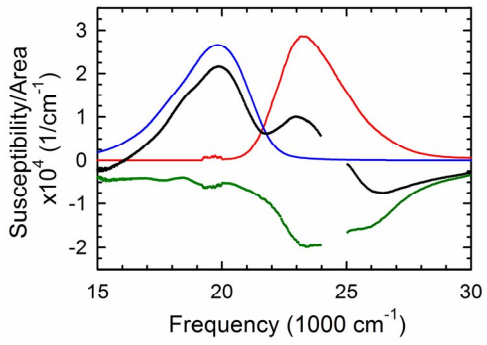

Figure S4. Transient absorption spectrum at 65 ps (black) decomposed into components using $\kappa = 1.45$: Transient absorption – black, stimulated emission – blue, ground-state bleach – red; excited-state absorption – green. Breaks in the transient and excited-state absorption occur where the spectra are contaminated by scattered excitation light.

the Stokes shift and broadening relative to the glass should be small or zero, but not negative. (3) The emission spectra should agree with up-conversion results, where they are available. Condition (3) was not used directly in analyzing the data, but rather, was used as a check on the validity of the final results (see Figure 2A).

The initial analysis assumed that the excited-state absorption is time-independent, $\chi_{EA}(\omega, t) = \chi_{EA}(\omega, 65\text{ ps})$. This assumption implies that the higher excited states and S_1have the same dipole moment and, as a result, have identical and canceling solvation shifts. With this assumption, it is difficult to satisfy both criteria (1) and (2) simultaneously and the agreement of up-conversion and stimulated-emission decays is poor.

We then explored the possibility that the higher excited states have a different dipole moment than S_1 and, as a result, show a time-dependent shift proportional to the shift of the emission Stokes shift $S(t)$

$$\chi_{ES}(\omega, t) = \chi_{ES}\left(\omega + b\left[S(t) - S(65\,\text{ps})\right], 65\,\text{ps}\right). \qquad \text{(S2)}$$

The time-dependent excited-state spectrum was found with an iterative procedure. An initial set of Stokes shifts was found with $b = 0$. These were used in eq S2 to generate an improved excited-state absorption spectrum. Using these spectra were then used in eq S1 to generate a new set of Stokes shifts. Convergence was found within a few iterations.

Good results were found with $b = 0.5$, and with κ in the range 1.3 – 1.5. The value $\kappa = 1.45$ was used in the final analysis. The resulting decomposition of the transient absorption spectrum at 65 ps is shown in Figure S4.

In the procedures described above, the emission spectra from both up-conversion and transient-absorption have been matched to the emission spectrum from TCSPC at 65 ps. However, the first moments calculated from these three spectra do not match perfectly. Each spectrum consists of points at different frequencies. As a result, the interpolations between these points and the extrapolations of the spectral tails are slightly different and there is a small but systematic difference between the calculated first moments. To correct for this shift, the first moments were matched at 65 ps by shifting the up-conversion data by +50 cm^{-1}; the transient absorption data did not need any adjustment.

Some portion of the Stokes-shift is due to vibration-like motions of the coumarin, DNA and solvent (inertial dynamics or inner-sphere reorganization); another part is due to more complex relaxations of the coumarin's environment that are driven by stochastic interactions with a bath (diffusive dynamics or outer-sphere reorganization).[5] The zero point of the Stokes-shift scale was taken from the emission spectrum of the sample frozen into a glass.[1] Because vibrational motions are still active in the glass, this scale eliminates their contribution to the Stokes shift. The fit to eq 1, which assumes $S(0) = 0$ on this scale, is consistent with the data, suggesting that only a small amount of diffusive dynamics occur before 40 fs. The tail of the inertial dynamics may affect the earliest points, but the majority of any inertial dynamics lie below our time resolution.

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(2) Horng, M. L.; Gardecki, J. A.; Papazyan, A.; Maroncelli, M. *J. Phys. Chem.* **1995**, *99*, 17311.
(3) Dobryakov, A. L.; Kovalenko, S. A.; Ernsting, N. P. *J. Chem. Phys.* **2003**, *119*, 988.
(4) Absorption and emission spectra are extrapolated to infinity as described in Ref. 1. The excited-state absorption is integrated from 14,600 – 33,400 cm-1.
(5) Carter, E. A.; Hynes, J. T. *J. Chem. Phys.* **1991**, *94*, 5961.