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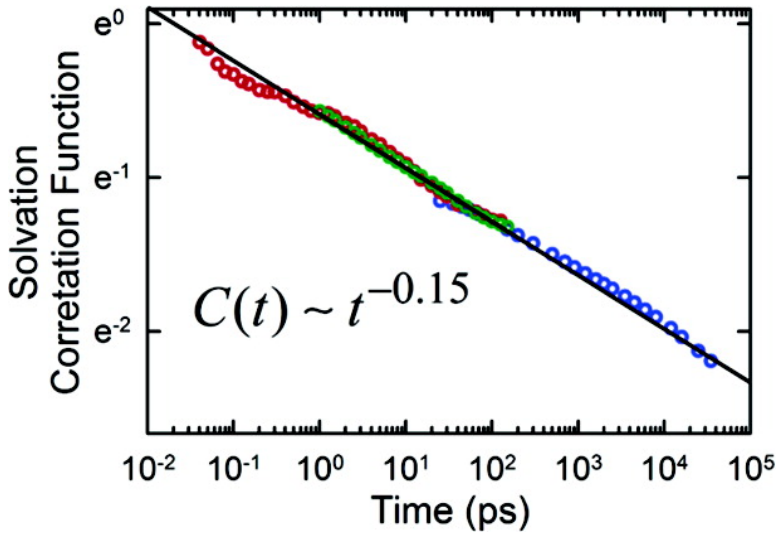

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Power-Law Solvation Dynamics in DNA over Six Decades in Time

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Chemical reactions occurring in solution are strongly affected by the surrounding solvent. For biochemical reactions occurring in DNA, these solvent effects are replaced by interactions with the complex DNA structure surrounding the reaction site. Charge transfer between DNA bases is one example of a reaction where these unusual "solvent" effects are especially important.[1] At least six papers in the past few years have modeled the effect of environmental reorganization on charge transfer in DNA.[2−7]

This paper presents experimental results on the time dependence of DNA reorganization that are unanticipated by any of these theoretical treatments. The reorganization follows power-law kinetics and is more like the dynamics of proteins[8] than the solvation dynamics of simple liquids. Solvation occurs faster than, on the same time scale as, and slower than the base-to-base electron transfer times in DNA. This result is important, not only for electron transfer but also for a variety of other fast processes in DNA.

In this paper, the concepts of polarity and solvation are extended to the complex structure of DNA. Polarity comprises a variety of processes by which a solvent or other matrix stabilizes charge within reactants, products, and transition states. Reactions in DNA are subject to charge stabilization from the motion of water molecules, counterions, phosphate groups, and DNA bases. The magnitude of this charge stabilization defines the effective "polarity" within DNA, and the time scale on which this stabilization develops defines the "solvation dynamics" within DNA.

To measure these effects, we use a well-known polarity sensitive dye, coumarin 102. It is synthetically incorporated into an oligonucleotide, where it replaces a native base pair.[9,10] Upon optical excitation, there is an intramolecular charge transfer within the coumarin. As the DNA reorganizes to stabilize this new charge distribution, it lowers the coumarin's excited-state energy. The reorganization is monitored by measuring the time-dependent shift (Stokes shift) of the coumarin emission spectrum toward lower frequency.

Three different techniques were used to measure the time-resolved emission spectrum: time-correlated single-photon counting from 40 ps to 40 ns,[11] fluorescence up-conversion from 1 to 150 ps, and transient absorption measurements from 40 fs to 120 ps (see Supporting Information). Measurements were made on the 17-mer 5′-GCATGCGC*CGCGTACG-3′ (* = coumarin) hybridized with its complement (abasic site analogue opposite coumarin) in pH 7, 100 mM sodium phosphate buffer.

Figure 1 shows emission spectra from all three techniques. The important feature of these data is that the Stokes shift increases continuously throughout the 40 fs to 40 ns time range.

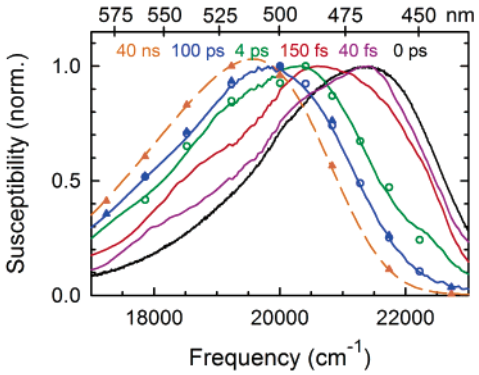

Figure 1. Examples of time-resolved emission spectra of coumarin 102 in DNA. Solid curves − emission component of transient absorption; open circles − fluorescence up-conversion; triangles and dashed curve − time-correlated single-photon counting. Right to left: black − glass (0 ps); purple − 40 fs; red − 150 fs; green − 4 ps; blue − 100 ps; orange − 40 ns.

The Stokes shifts $S(t)$ derived from all three techniques are presented on a logarithmic time scale in Figure 2A. Over the entire six decade time range, a simple three-parameter formula

$$S(t) = S_\infty[1 - (1 + t/t_0)^{-\alpha}] \qquad (1)$$

with the values $S_\infty = 2086$ cm^{-1}, $\alpha = 0.15 \pm 0.03$, and $t_0 = 19$ fs fits the data. For comparison, a biexponential and a strongly stretched exponential ($\beta = 0.3$) are also shown. Neither of these common decay forms describe the data well.

Power-law kinetics are unusual, but do occur in a number of complex systems ranging from spin glasses to the growth of organisms. Power-law kinetics with an exponent of 3/2 are found in problems involving molecular diffusion in three dimensions (or 1/2 in one dimension).[12] Proteins are perhaps the most closely related systems where power-law relaxation occurs.[8] However, there is not a general theory for the origin of power-law kinetics, and it is not clear how to make a connection between solvation in DNA and these other processes.

DNA reorganization is not complete by the end of the experimental time range. However, $S_\infty = 2086$ cm^{-1} is an extrapolated estimate of the equilibrium Stokes shift. The zero point of the Stokes shift scale is set to the position of the emission in a frozen, glassy matrix. This scale measures the solvation by processes other than vibrations of the coumarin, DNA, or solvent (see Supporting Information). By these estimates, the current experiments observe 70% of the total nonvibrational Stokes shift (from 85 to 15%).

In simple solvents, the equilibrium Stokes shift of coumarin 102 is a good measure of the solvent polarity. Using the Stokes shift of coumarin 102 in ethanol as a calibration point,[11] the effective

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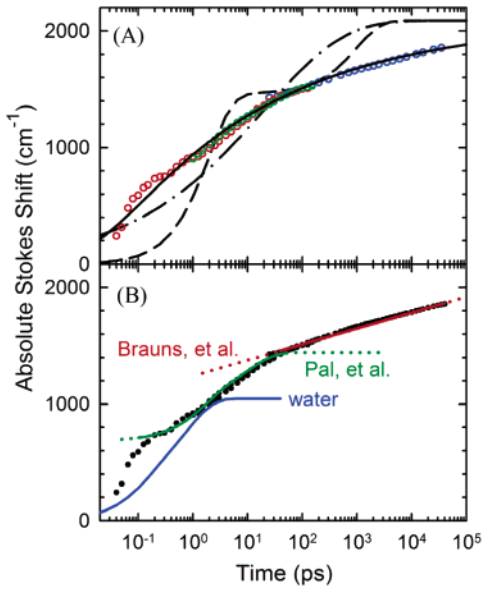

Figure 2. Time-resolved Stokes shift data. (A) Measurements from three techniques fit to a power law (eq 1, solid): blue − time-correlated single-photon counting; green − fluorescence up-conversion; red − transient absorption. For comparison, a biexponential (dashed) and a stretched exponential ($\beta = 0.3$, dot−dashed line) are shown on the same scale. (B) The same data (points) compared to previous work (measured region − solid, extrapolation − dotted): red − logarithmic fit at long times;[13] green − biexponential fit at intermediate times;[14] blue − solvation of pure water.[15]

polarity of DNA is 0.69 on the E_T^N polarity scale. Despite being buried in the hydrophobic core of the DNA, the coumarin experiences a total charge stabilization similar to that occurring in polar solvents, such as ethanol ($E_T^N = 0.65$) or formamide ($E_T^N = 0.78$), although the stabilization in DNA is less than that in pure water ($E_T^N = 1.00$).

Although the magnitude of the polarity is similar in DNA and in simple solvents, the solvation dynamics are very different. The solvation correlation function corresponding to eq 1 is

$$C(t) = \frac{S_\infty - S(t)}{S_\infty} = (1 + t/t_0)^{-\alpha} \qquad (2)$$

The dynamics are characterized by a single parameter α. The time t_0 only governs the switch from power-law kinetics $C(t) \propto t^{-\alpha}$ at long time to $C(0) = 1$ at short time. This switch is required theoretically, but is not directly observed in these experiments.[16]

In Figure 2B, our data are compared to previous results over smaller time ranges. Using only results over the 40 ps to 40 ns range, we had reported a logarithmic time dependence, that is, linear on a logarithmic time scale. The logarithmic form is the limit as $\alpha \rightarrow 0$ of the power-law decay. The current result is an improved measurement of the small, nonzero value of α.

Zewail and co-workers measured the time-resolved Stokes shift of 2-aminopurine in an oligonucleotide over the 100 fs to 50 ps time range and fit their data to a biexponential.[14] The faster exponential was assigned to unperturbed water and the slower one to "biological water".

The fit of Zewail and co-workers is shown in Figure 2B, shifted and rescaled to account for the difference in probe molecules. Over the time range of their measurement, there is no significant disagreement with our measurements, despite differences in the details of the sample conditions. This result suggests that we are both looking at general features of DNA, not details of our specific samples or peculiarities of the specific probe molecules.

The biexponential fit and the power-law fit are difficult to distinguish over a limited time range. However, with our broader data set, the biexponential model no longer fits. In particular, our data show a smooth time dependence without a distinct component attributable to biological water.

Figure 2B also compares DNA solvation dynamics to the noninertial solvation dynamics of pure water, as measured by Fleming and co-workers.[15] To account for shielding of the water response by the DNA, the amplitude has been adjusted for comparison to our data.

Although the fastest components of the solvation in DNA are nearly as fast as the solvation dynamics in pure water, there is not a distinct component in DNA that is attributable to an unperturbed water response. A large portion of the total Stokes shift is slower than the water response. This fact suggests that motion of components other than water (ions, DNA backbone, and DNA bases) play an important role in the solvation response.

The origin of power-law dynamics in DNA and the small value of the power-law exponent present a challenge to the theory of DNA behavior. The fact that the dynamics extend over a very broad time range suggests that many different components of the system are contributing to the solvation response. However, the smooth relaxation and lack of discernible subcomponents suggest that the motions of different portions of the DNA system are strongly coupled. In this case, the dynamics of the system must be treated as a collective response of the whole system, not as the sum of several independent processes.

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Supporting Information Available: Additional figures and data calculation and analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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