Thermal Fluctuations and Charge-Transfer Dynamics in 2-Aminopurine-Labeled DNA JOHN JEAN, Washington University — We present results from picosecond fluorescence experiments and hybrid TDDFT/molecular dynamics simulations that examine the roles of rapid fluctuations in base-stacking interactions on both charge transfer and electronic energy transfer dynamics in single-stranded DNA trimers containing a central 2AP. Direct excitation of the 2AP $\pi-\pi^*$ state shows that in these highly flexible systems, the 2AP $\rightarrow$ X charge transfer process occurs on timescales ranging from $<50$ ps to several ns. The dependence of the fluorescence decays on temperature and viscosity suggest that those trimers that are optimally stacked undergo rapid CT leading to a nonequilibrium “hole” in the conformational distribution. Diffusion of bases back into a stacked conformation plays a critical role in determining the long-time decays. Energy transfer (A $\rightarrow$ 2AP) in these systems occurs on the timescale of $\sim1$ picosecond. The energy transfer efficiency shows little dependence on solution viscosity over the range of 1-15 cP, suggesting that the large amplitude structural fluctuations that are important in the CT dynamics are “frozen out” on the EET timescale. These results are supported by TDDFT/MD simulations of the dynamic electronic coupling between 2AP and its flanking bases. Using a modified Forster approach, which incorporates the full multipole-multipole coupling between bases, we examine the sensitivity of the EET rates to conformational fluctuations and compute the ensemble-averaged (steady-state) transfer efficiency.

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