# DNA Charge Transport: Conformationally Gated Hopping through Stacked Domains

**Melanie A. O'Neill and Jacqueline K. Barton***

*Contribution from the Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125*

jkbarton@caltech.edu

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**Abstract:**

The role of base motions in delocalization and propagation of charge through double helical DNA must be established experimentally and incorporated into mechanistic descriptions of DNA-mediated charge transport (CT). Here, we address these fundamental issues by examining the temperature dependence of the yield of CT between photoexcited 2-aminopurine (Ap*) and G through DNA bridges of varied length and sequence. DNA assemblies (35-mers) were constructed containing adenine bridges $Ap(A)_nG$ ($n$ = 0-9, 3.4-34 Å) and mixed bridges, ApAAIAG and ApATATG. CT was monitored through fluorescence quenching of Ap* by G and through HPLC analysis of photolyzed DNA assemblies containing Ap and the modified guanine, $N^2$-cyclopropylguanosine ($^{CP}$G); upon oxidation, the $^{CP}$G radical cation undergoes rapid ring opening. First, we find that below the duplex melting temperature (~60 °C), the yield of CT through duplex DNA increases with increasing temperature governed by the length and sequence of the DNA bridge. Second, the distance dependence of CT is regulated by temperature; enhanced DNA base fluctuations within duplex DNA extend CT to significantly longer distances, here up to 34 Å in <10 ns. Third, at all temperatures the yield of CT does not exhibit a simple distance dependence; an oscillatory component, with a period of ~4-5 base pairs, is evident. These data cannot be rationalized by superexchange, hopping of a localized charge injected into the DNA bridge, a temperature-induced transition from superexchange to thermally induced hopping, or by phonon-assisted polaron hopping. Instead, we propose that CT occurs within DNA assemblies possessing specific, well-coupled conformations of the DNA bases, CT-active domains, accessed through base motion. CT through DNA is described as conformationally gated hopping among stacked domains. Enhanced DNA base motions lead to longer range CT with a complex distance dependence that reflects the roles of coherent dynamics and charge delocalization through transient domains. Consequently, DNA CT is not a simple function of distance but is intimately related to the dynamical structure of the DNA bridge.

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