

Direct simulation of electron transfer reactions in DNA radical cations

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Abstract

The electron transfer properties of DNA radical cations are important in DNA damage and repair processes. Fast long-range charge transfer has been demonstrated experimentally, but the subtle influences that experimental conditions as well as DNA sequences and geometries have on the details of electron transfer parameters are still poorly understood. In this work, we employ an atomistic QM/MM approach, based on a one-electron tight binding Hamiltonian and a classical molecular mechanics forcefield, to conduct nanosecond length MD simulations of electron holes in DNA oligomers. Multiple spontaneous electron transfer events were observed in 100 ns simulations with neighboring adenine or guanine bases. Marcus parameters of charge transfer could be extracted directly from the simulations. The reorganisation energy λ for hopping between neighboring bases was found to be ca. 25 kcal/mol and charge transfer rates of $4.1 \times 10^9 \text{ s}^{-1}$ for AA hopping and $1.3 \times 10^9 \text{ s}^{-1}$ for GG hopping were obtained.