

Theoretical Rate Constants of Super-Exchange Hole Transfer and Thermally Induced Hopping in DNA

Tomomi Shimazaki,[†] Yoshihiro Asai,^{†,‡} and Koichi Yamashita,[†]

[†]*Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo,
Tokyo 113-8656, Japan*

[‡]*RICS, Fundamental analysis research group*

Recently, the electronic properties of DNA have been extensively studied, because its conductivity is important not only to the study of fundamental biological problems, but also in the development of molecular-sized electronics and biosensors. We have studied theoretically the reorganization energies, the activation energies, the electronic coupling matrix elements, and the rate constants of hole transfer in B-form double-helix DNA in water. To accommodate the effects of DNA nuclear motions, a subset of reaction coordinates for hole transfer was extracted from classical molecular dynamics (MD) trajectories of DNA in water and then used for ab initio quantum chemical calculations of electron coupling constants based on the generalized Mulliken-Hush model. A molecular mechanics (MM) method was used to determine the nuclear Franck-Condon factor. The rate constants for two types of mechanisms of hole transfers—the thermally induced hopping (TIH) and the super-exchange mechanisms were determined based on Marcus theory. We found that the calculated matrix elements are strongly dependent on the conformations of the nucleobase pairs of hole-transferable DNA and extend over a wide range of values for the “rise” base-step parameter but cluster around a particular value for the “twist” parameter. The calculated activation energies are in good agreement with experimental results. Whereas the rate constant for the TIH mechanism is not dependent on the number of A-T nucleobase pairs that act as a bridge, the rate constant for the super-exchange process rapidly decreases when the length of the bridge increases. These characteristic trends in the calculated rate constants effectively reproduce those in the experimental data of Giese et al. [*Nature* **2001**, *412*, 318]. The calculated rate constants were also compared with the experimental results of Lewis et al. [*Nature* **2000**, *406*, 51].

Reference:

T. Shimazaki, Y. Asai and K. Yamashita, *J. Phys. Chem. B* **109**, 1295 (2005).