

Heterogeneous Electron Transfer Reactions inside Carbon Nanotubes: Molecular Dynamics Simulations

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Molecular details of the electron transfer (ET) elementary act in confined systems like nanopores, are interesting but challenging to obtain. Two recent attempts to elucidate the kinetics of simple redox couples in solvent-filled nanopores using molecular dynamics (MD) simulations [1, 2] led to contradictive results; an enhancement of the ET rate under nano-confined conditions was predicted in [1], whereas a rate decrease compared with bulk solution has been reported in [2].

We investigated systematically the heterogeneous kinetics of a $\text{Fe}^{3+/2+}$ redox couple in carbon nanopores in an aqueous environment. Conducting single-walled carbon nanotubes with diameters from 0.8 to 3.5 nm serve as a model of pores. Molecular dynamics simulations were performed using the LAMMPS program package [3]. The SPC/E model describes water while the CHARMM force field [4] and the $\text{Fe}^{3+/2+}$ -H₂O potentials devised in [5] are used for the other interactions. We analyse primarily the solvent reorganization energy which is calculated at several ion-wall separations. This is performed by constructing two reaction free energy surfaces along the solvent coordinate. The influence of the image charge on the reorganization energy could be investigated after solving this electrostatic problem for a perfectly conducting cylinder. Axial and radial components of the static dielectric constant are also presented [6].

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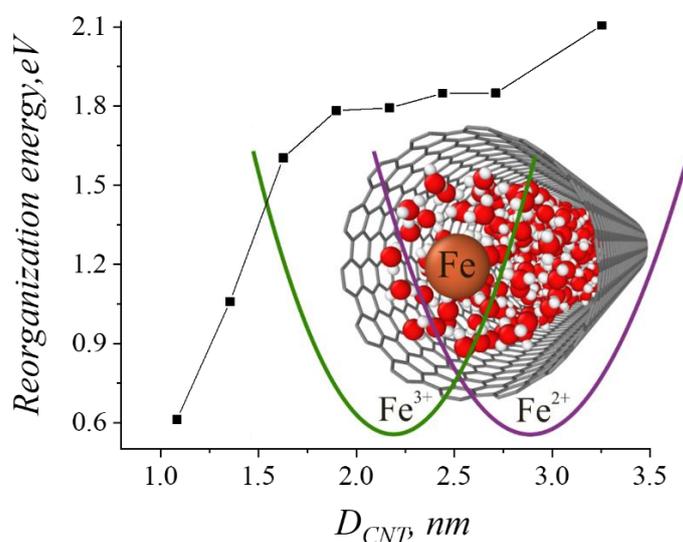


Figure 1: Reorganization energy calculated from free energy surfaces and visualization of the Gibbs energy surfaces for heterogeneous electron transfer along the solvent coordinate