

Coherent and Incoherent Electron Transport through Protein Junctions Investigated by DFT-based Approaches

Z. Futera

Faculty of Science, University of South Bohemia, Branišovská 1760,
370 05 České Budějovice, Czech Republic
e-mail: zfutura@prf.jcu.cz

INTRODUCTION

Electron transfer facilitated by redox-active proteins is utilized in various biological processes, including photosynthesis, respiration cycle, or denitrification reactions. Copper proteins such as Plastocyanin or Azurin and the heme-containing cytochromes often participate in these redox cascades. Recently, these proteins started to be utilized in nanobioelectronic devices due to their suitable electron-transfer properties. However, non-expected physical phenomena were observed when the proteins were incorporated between metal contacts or electrodes. While in a native aqueous environment, the electron flow through the system of redox sites proceeds by the thermally activated hopping mechanism, the temperature-independent currents of relatively high magnitudes were detected on protein/metal junctions. [1], [2] These data suggest that the electrons through protein junctions are transferred by the coherent tunneling mechanism, independently of the redox-active states.

METHODOLOGY

We investigate these electron-transport phenomena by means of computer simulations based on classical molecular dynamics (MD) as well as the first-principles description within the framework of density functional theory (DFT). [3], [4] While the incoherent hopping could be studied by combined quantum-mechanical/molecular-mechanical (QM/MM) techniques, [5] the coherent tunneling requires a quantum description of the whole interface models. Special care is taken to electronic-state alignment on the bio/metallic interfaces for which we apply the DFT+ Σ scheme.

RESULTS

We applied these methodologies on Azurin blue-copper protein and on small tetraheme cytochrome (STC), which were previously studied experimentally. We showed that the transport mechanism in both Azurin and STC junctions between gold electrodes is the coherent tunneling facilitated by valence-band states of the proteins. In contrast to their redox properties in solution, the presence of the metal cations in the protein structures is not essential for their conductivity on the metal interfaces. The reason for this drastically different behavior in solution and on the metal interfaces is the significant electronic-level misalignment between the protein and metallic states. [6] However, the state position, and so the transport mechanism, can be modulated by application of gating potentials.

REFERENCES

- [1] K. Garg *et al.*, *Direct Evidence for Heme-Assisted Solid-State Electronic Conduction in Multi-Heme c-Type Cytochromes*. *Chem. Sci.* **9**, 7304 (2018)
- [2] Z. Futera *et al.*, *Coherent Electron Transport across a 3 nm Bioelectronic Junction Made of Multi-Heme Proteins*. *J. Phys. Chem. Lett.* **11**, 9766 (2020)
- [3] D. Biriukov, Z. Futera *Adsorption of Amino Acids at the Gold/Aqueous Interface: Effect of an External Electric Field*. *J. Phys. Chem. C* **125**, 7856 (2021)
- [4] Z. Futera, *Amino-Acid Interactions with the Au(111) Surface: Adsorption, Band Alignment, and Interfacial Electronic Coupling*. *Phys. Chem. Chem. Phys.* **23**, 10257 (2022)
- [5] O.V. Kontkanen, D. Biriukov, Z. Futera *Reorganization Free Energy of Copper Proteins in Solution, in Vacuum, and on Metal Surfaces*. *J. Chem. Phys.* **156**, 175101 (2022)
- [6] Z. Futera, X. Wu, J. Blumberger *Tunneling-to-Hopping Transition in Multiheme Cytochrome Bioelectronic Junctions*. *J. Phys. Chem. Lett.* **14**, 445 (2023)

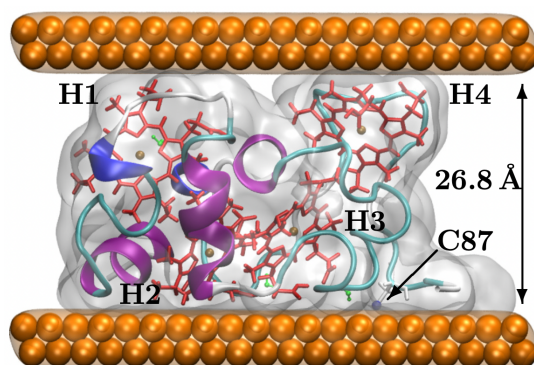


Fig. 1. Model of the STC junction with indicated position of the four redox heme cofactors and chemisorbed Cys87 site. [2]

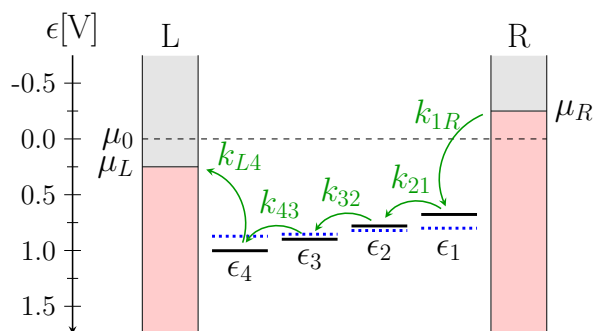


Fig. 2. Schematic illustration of incoherent electron hopping events through four STC redox sites between left (L) and right (R) metal contacts. [6]

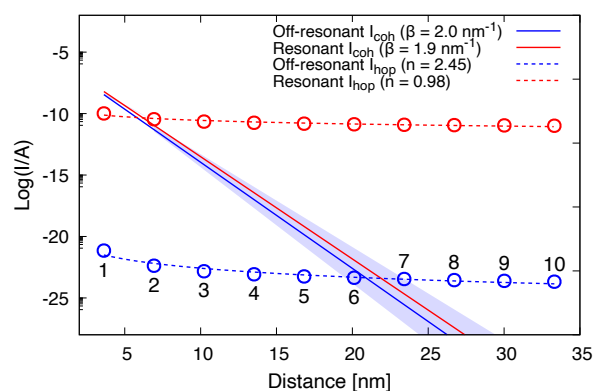


Fig. 3. Distance dependencies of coherent (I_{coh}) and incoherent (I_{hop}) current in multi-STC junctions. [6]