

ELECTRON TUNNELING AND HOPPING THROUGH PROTEINS

Thesis by

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A C K N O W L E D G M E N T S

I've loved science ever since I was in the third grade, but as I also "loved" New Kids on the Block, my opinion was not really to be trusted. However unwise I was in some choices, I had fantastic teachers, among them Karen Wickersham, Heston Bates, and Ross Graham, to take my interest and root it in science.

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*This thesis is dedicated to my Mom and Dad,
for being the best inspiration a person could have.*

THEESIS ABSTRACT

Long-range electron tunneling is a central component of processes that are essential for biological function. While many studies have been made to understand electron transfer in proteins, biologically efficient electron transfer at distances exceeding 25 Å remains unobserved in these experiments and hence unresolved. It is proposed that long-range electron transfer is in actuality multistep electron tunneling. What is reported in this thesis is the design, synthesis, and study of many protein systems for the purpose of studying multistep electron tunneling in azurin.

In each system, a histidine has been introduced on the protein for attachment of a high-potential ruthenium or rhenium sensitizer ($[\text{Ru}(\text{trpy})(\text{tfmbpy})]^{2+}$ or $[\text{Re}(\text{dmp})(\text{CO})_3]^+$); a nitrotyrosine, tryptophan, or tyrosine is placed between the two metal centers on the tunneling pathway. The electron transfer is triggered with the excitation of the metal label with laser light, and the kinetics are monitored, for the most part, by time-resolved UV-VIS spectroscopy.

The first system to empirically demonstrate multistep electron tunneling in proteins was discovered; ultrafast electron transfer is observed between the copper and rhenium centers in the Re124/W122 system; the system was structurally characterized and studied by time-resolved UV-VIS and IR spectroscopies. A two-step tunneling model is proposed; the data sets for the different methods utilized are all in excellent agreement with the model.

Systematic perturbations were made to the working hopping system. It was discovered that nitrotyrosine can participate as an intermediate, but studies to

demonstrate its participation in multistep tunneling are not yet fully realized. A second hopping system was discovered in the development of the Re126/W122 system.

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