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Education

Post-Doc (1983-1985): Brookhaven National Laboratory
Ph.D. (June, 1984): California Institute of Technology
B.S. (June, 1978): Stanford University

Academic Carrier

1985-1987: Assistant Scientist, Brookhaven National Laboratory
1987-1990: Associate Scientist, Brookhaven National Laboratory
1990-: Member of the Beckman Institute, California Institute of Technology
1990-: Director, Beckman Institute Laser Center, California Institute of Technology
2002, 2004, 2009-: Lecturer, Division of Chemistry and Chemical Engineering, California Institute of Technology
2003: Lecturer, Department of Chemistry, University of California, Irvine
2008-: Faculty Associate in Chemistry, California Institute of Technology

Awards and Honors

Honda-Fujishima Lectureship Award, Japanese Photochemistry Association (2010)

Total Publications

180 Publications

Research Interests

My research program is an interdisciplinary experimental effort aimed at fundamental problems in biophysics, biochemistry, and inorganic chemistry. Steady-state and time-resolved laser spectroscopies play a central role in the development of new methods for studying chemical kinetics and reactive intermediates. In the mid 1990s, we initiated a research program to investigate the kinetics of metalloprotein folding triggered by electron transfer (ET). We demonstrated that this approach can be applied to a wide variety of redox-active proteins, permitting investigations of folding dynamics on microsecond (and faster) timescales. We also employ light-driven electron-transfer chemistry to study redox enzymes. Targets include electron transfer proteins (cytochromes, blue copper proteins), as well as multielectron redox enzymes (cytochrome P450, nitric oxide synthase). The objective of these investigations is to develop deeper insight into the mechanisms of long-range electron transfer and multi-electron redox reactions. One of the primary challenges in solar fuels research is to couple photodriven one-electron transfer processes to the multielectron redox chemistry that is required for long-term energy storage. We are employing laser flash-quench triggering methods, and time-resolved spectroscopic monitoring to map out the key steps as well as identify reactive intermediates in these critical transformations.

Electronic Coupling in Long-Range Electron Transfer

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The specific rates of nonadiabatic electron transfers (ET) depend on the strength of the electronic coupling between reactants and products at the transition state nuclear configuration. Theoretical models predict that this coupling depends on the distance between electron donor and acceptor, the structure and composition of the intervening medium, and the energy gap between the tunneling electron and hole and electron states of this medium. We have been investigating experimentally the factors that determine long-range electron-transfer coupling strengths in model complexes and proteins.¹ Comparison to data in the literature reveals that electronic couplings across protein media correlate well with those extracted from kinetics measurements in small molecules (Figure 1).²⁻⁴ The couplings inferred from optical intervalence ET and magnetic measurements tend to be greater at a given donor-acceptor separation than those derived from kinetics studies.⁵⁻⁷

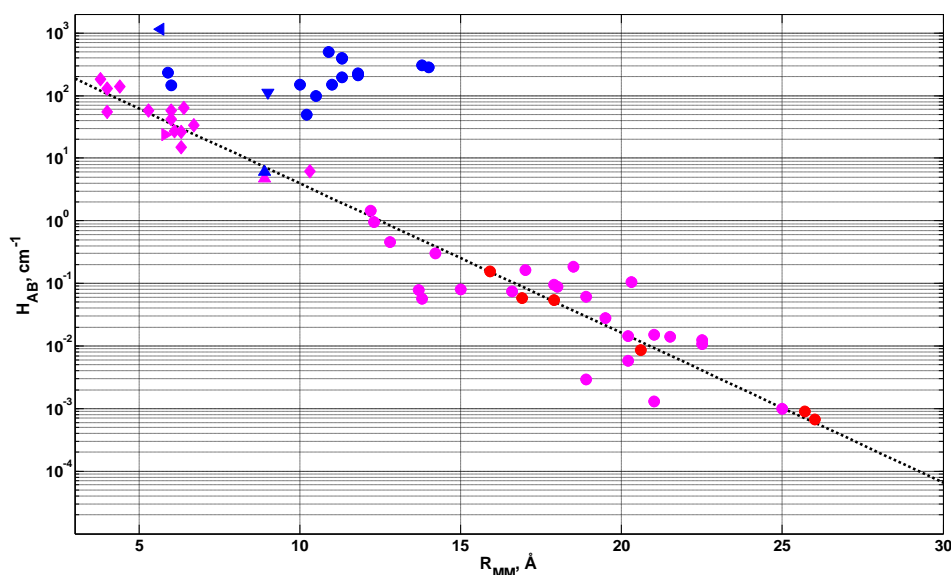


Figure 1. Distance dependence of electronic coupling strengths: ET kinetics in Ru-modified proteins;¹ rate measurements on Ir dimers;² kinetics and optical measurements on Fe dimers;³ ET kinetics in organic radical anions;⁴ optical ET in Ru dimers;^{5,6} optical ET and magnetic measurements in organic radicals.⁷

References

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4. Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*, 3673-3683.
5. Stein, C. A.; Taube, H. *J. Am. Chem. Soc.* **1981**, *103*, 693-695.
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